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Synthesis and Electronic Properties of Nanophase Semiconductor Materials

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

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13. ABSTRACT (*Maximum 200 words*)

The objective of the research effort is to understand and learn to control the morphologic and electronic properties of electrodeposited nanophase semiconductors. The initial work has focused on electrodeposition of nanophase CdSe, using a sequential monolayer deposition technique that we are developing. We are currently extending the synthesis phase of this project into silicon, silicon carbide, and phosphor materials. This work also encompasses studying semiconductor electrodeposition into materials with restricted dimensions, such as microporous alumina and porous silicon membranes. By growing films with very small grain sizes, we hope to produce and study materials that display unusual electronic or luminescent effects. We are primarily interested in the electronic properties of the II-VI and group IV materials, for potential applications in nanoscale electronics and optical detector technologies. The phosphors are being studied for their potential as efficient high-resolution display materials.

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END-OF-THE-YEAR REPORT

PUBLICATIONS / PATENTS / PRESENTATIONS / HONORS / STUDENTS REPORT

for

Contract N00014-92J-1810

R&T CODE: 4133040

Synthesis and Electronic Properties of Nanophase Semiconductor Materials

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May 25, 1993

OFFICE OF NAVAL RESEARCH
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS REPORT

R&T Number: 4133040
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b. * Number of papers published in refereed journals (for each, provide a complete citation): 2
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e. * Number of printed technical reports/non-refereed papers (for each, provide a complete citation): _____
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including the number of,
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Female Post-Doctoral Associates: 0
the number of
Minority* Graduate Students: 0
Minority* Post-Doctoral Associates: 0
and, the number of
Asian Graduate Students: 1
Asian Post-Doctoral Associates: 0
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b. Published Papers in Refereed Journals, or, d. Books and Chapters published
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* Minorities include Blacks, Aleuts, AmIndians, Hispanics, etc. NB: Asians are not considered an under-represented or minority group in science and engineering.

PART I

a. *Papers submitted to refereed journals, but not published:*

"Electrochemical Fabrication of Cadmium Chalcogenide Microdiode Arrays" Jonathan D. Klein, Robert D. Herrick II, Dean Palmer, Charles J. Brumlik, Charles R. Martin, and Michael J. Sailor. Accepted for publication, *Chemistry of Materials*.

"Observation of Optical Cavity Modes in Photoluminescent Porous Silicon Films." Corrine L. Curtis, Vincent V. Doan, Grace M. Credo, and Michael J. Sailor. Submitted for publication, *Journal of the Electrochemical Society*.

"Chemical Modification of The Photoluminescence Quenching Behavior of Porous Silicon," Jeffrey M. Lauerhaas and Michael J. Sailor. Submitted for publication, *Science*.

b. *Papers Published in Refereed Journals:*

"Enhanced Photoemission from Short-Wavelength Photochemically Etched Porous Silicon" Vincent V. Doan, Reginald M. Penner and Michael J. Sailor, *J. Phys. Chem.* **1993**, *97*, 4505-4508.

"Photoluminescent thin-film porous silicon on sapphire" W.B.Dubbelday, Diane M. Szaflarski, R.L. Shimabukuro, S.D. Russell and Michael J. Sailor, *Appl. Phys. Lett.* **1993**, *62(14)*, 1694-96.

h. *Invited Presentations:*

"Surface Modification Of Photoluminescent Porous Silicon" Jessica Harper, J. L. Heinrich, J. M. Lauerhaas And M. J. Sailor, Presented at the *Chemical Change at Surfaces* Symposium at the 1993 Spring ACS meeting, Denver, CO.

"Chemical Manipulation Of The Properties Of Photoluminescent Porous Silicon" Jessica Harper, J. L. Heinrich, J. M. Lauerhaas And M. J. Sailor, *Silicon-Based Optoelectronic Materials* , 1993 Meeting of the Materials Research Society, San Francisco, CA.

i. *Submitted Presentations,*

"Cadmium Chalcogenide Diode Arrays in a Microporous Membrane" Jonathan D. Klein, Robert D. Herrick II, Dean Palmer, Charles J. Brumlik, Charles R. Martin, and Michael J. Sailor, presented in the Colloid and Surface Division of the 1993 Spring ACS meeting, Denver, CO.

"Enhanced Luminescence And Optical Cavity Modes From Uniformly Etched Porous Silicon," Vincent V. Doan, C. L. Curtis, G. M. Credo, R. M. Penner, and M. J. Sailor Mat. Res. Soc. Symp. Proc., *Silicon-Based Optoelectronic Materials* , 1993 Meeting of the Materials Research Society, San Francisco, CA.

"The Effects Of Halogen Exposure On The Photoluminescence Of Porous Silicon" Jeffrey M. Lauerhaas And Michael J. Sailor, Mat. Res. Soc. Symp. Proc., *Silicon-Based Optoelectronic Materials* , 1993 Meeting of the Materials Research Society, San Francisco, CA.

j. *Honors/awards/prizes*

Beckman Young Investigator Award 1993

k. *Total number of FTE's*

1.	Corrine Curtis	graduate	female
2.	Vinh Doan	graduate	asian

l. *Other Funding:*

ACS-PRF G ~ 24077-G3
Studies Of Inorganic Complexes Of Soluble Electronically Conductive Polymers
07/01/91 - 08/31/93 $ 21,000
No relationship to ONR grant

NSF DMR DMR-9220367
Chemistry Of Luminescent Porous Si
04/01/93 - 01/31/96 $ 238,699
This grant now covers all our work on luminescent porous silicon

PART II

a. *Principal Investigator:* Michael J. Sailor
b. *Current telephone number:* (619) 534-8188
c. *Cognizant ONR Scientific Officer:* Dr. Robert Nowak

d. *Description of Project:*

The objective of the research effort is to understand and learn to control the morphologic and electronic properties of electrodeposited nanophase semiconductors. The initial work has focused on electrodeposition of nanophase CdSe, using a sequential monolayer deposition technique that we are developing. We are currently extending the synthesis phase of this project into silicon, silicon carbide, and phosphor materials. This work also encompasses studying semiconductor electrodeposition into materials with restricted dimensions, such as microporous alumina and porous silicon membranes. By growing films with very small grain sizes, we hope to produce and study materials that display unusual electronic or luminescent effects. We are primarily interested in the electronic properties of the II-VI and group IV materials, for potential applications in nanoscale electronics and optical detector technologies. The phosphors are being studied for their potential as efficient high-resolution display materials.

e. *Significant results during last year:*

- Fabrication and electrical characterization of the largest parallel diode arrays yet made ($>10^9$ diodes/cm^2), via electrodeposition of CdSe into the pores of Anopore alumina membranes.

- Extension of the Sequential Monolayer Deposition technique to the synthesis of CdTe films.

- Fabrication of CdSe/CdTe heterojunction arrays using the above techniques.

f. Summary of plans for next year's work:

We will continue our investigation of the electronic properties and morphology of semiconductor films electrodeposited into restricted dimensions. Two curious results that we wish to pursue are: (1) CdSe and CdTe Films deposited in these restricted dimensions do not grow with the fractal-like ("cauliflower") morphology of normally electrodeposited films. This result could enable the synthesis of more uniform thin films for solar energy or optical detector applications. (2) There appears to be a pronounced effect on the properties of these films when deposited under optical irradiation. We will try to exploit this effect to produce more electronically well-behaved materials.

We will try to extend our electrochemical synthesis to the deposition of Si and SiC materials. Because of its refractory nature, SiC is hard to manufacture, although it is the only material currently used commercially to manufacture blue light emitting diodes. The approach will involve non-aqueous deposition onto conductive single-crystal substrates.

We are also investigating the feasibility of depositing ZnS-based phosphor materials into Anopore and other template membranes, for potential high-definition display applications.

g. Students currently working on the project:

Corrine Curtis (Graduate student)

Robert Herrick (Undergraduate)

James Gerkin (Undergraduate)

Vinh Doan (Graduate Student)

PART III

a. Introductory vu-graph

b. Figure representing the highlight

c. Concluding vu-graph

d. "Synthesis and Electronic Properties of Nanophase Semiconductor Materials"
Michael J. Sailor UCSD Department of Chemistry

An array of over a billion parallel, 200 nm-diameter wires of CdSe can be synthesized within the pores of an alumina template membrane. These wires show a nonlinear current-voltage response characteristic of rectifying diodes, and hence this work demonstrates the largest diode array ever fabricated. The CdSe rods are made by electrochemically depositing the material onto a Ni electrode that is covered with a porous Al_2O_3 filtration membrane. Both CdSe and CdTe nanowires can be fabricated from the appropriate deposition bath, and CdSe/CdTe heterojunction arrays can also be made by this technique.

Semiconductor Thin Films by Electrodeposition

Motivations

- Nanoscale Crystallites-Quantum Effects

  Electrochemically deposited materials usually deposit as fine nanocrystalline films
- Low Temperature Phases

  Thermodynamic phases obtained from electrodeposition often differ from thermally grown materials
- Inexpensive, Large Area - Microelectronics & Solar Cells

  Electrodeposition provides thickness and morphology control-can fabricate unusual structures

Problems

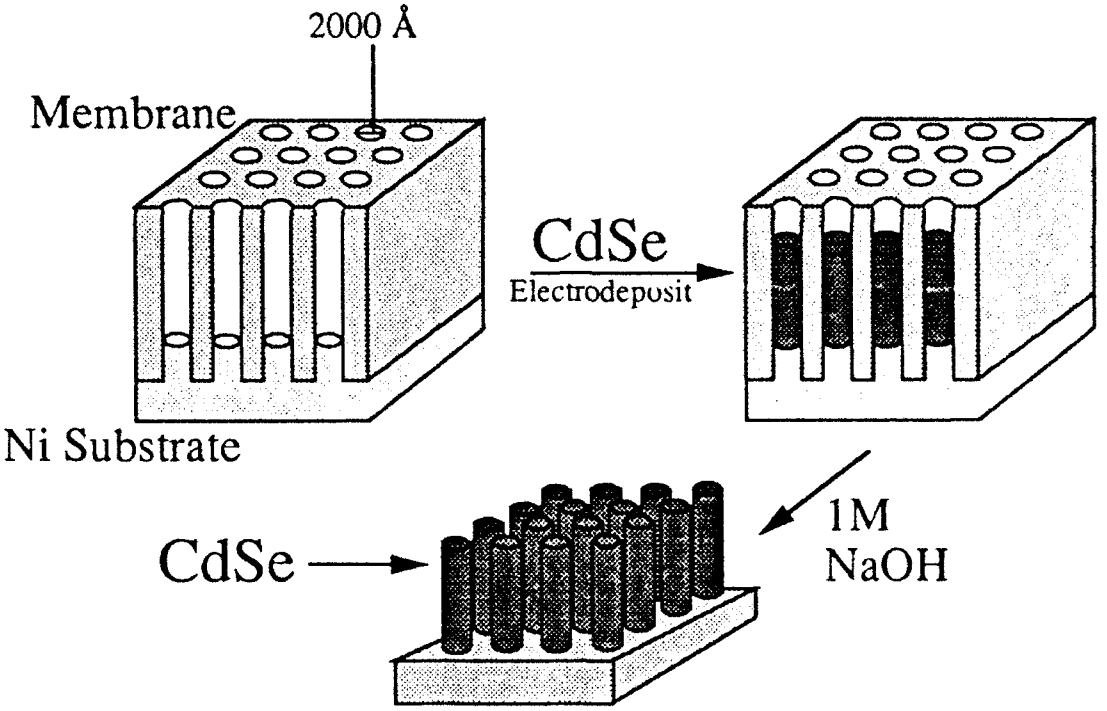
- Stoichiometry *is often nonideal*
- Morphology *is often fractal-like*
- Electronic *properties are inferior*

One Approach–Deposition Within Restricted Dimensions

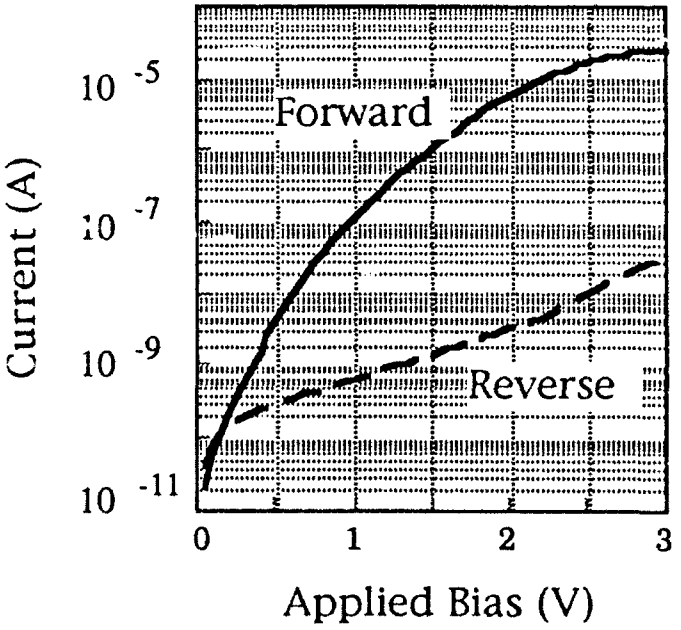
Electrodeposit CdSe into nanoporous alumina membrane

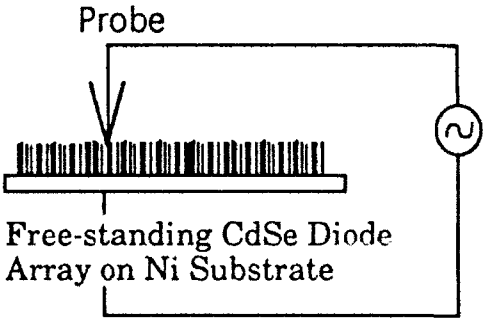
- Growth morphology is restricted to (pseudo) one dimension-provides shape control
- Stoichiometry is controlled using a specialized pulse-plating technique

Electrochemical Fabrication of Cadmium Chalcogenide Microdiode Arrays.



Current-Voltage Characteristic:





"Synthesis and Electronic Properties of Nanophase Semiconductor Materials"--Michael J. Sailor
UCSD Department of Chemistry

Electrochemical Fabrication of Cadmium Chalcogenide Microdiode Arrays.

From "S. .thesis and Electronic Properties of Nanophase Semiconductor Materials"--Michael J. Sailor UCSD Department of Chemistry

Conclusions:

- Arrays containing $>10^9$ 2000Å-diameter CdSe or graded CdSe/CdTe cylinders have been electrochemically synthesized within the pores of Anopore™ membranes. This represents the largest diode array yet produced.
- The alumina template suppresses the 'cauliflower' morphology that is typically observed in electrodeposited CdSe and CdTe films.
- Current-Voltage data show that the Ni/CdSe array is rectifying, with a rectification ratio of 1000 at $\pm$ 2 V.
- These results may be important for the fabrication of high-resolution optical detectors, solar cells, or high-definition displays.