OFFICE OF NAVAL RESEARCH

END-OF-THE-YEAR REPORT

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

for

GRANT or CONTRACT: N000149410302

PR NUMBER: 97PR02971-00

19970707 045

"Organized Nanorod-Superconductor Composites"

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Date Submitted:
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PR Number: 97PR02971-00
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Contract/Grant Title: "Organized Nanorod-Superconductor Composites"
Principal Investigator: Charles M. Lieber
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a. • Number of papers submitted to refereed journals, but not published: 3
b. • Number of papers published in refereed journals (for each, provide a complete citation): 5
c. • Number of books or chapters submitted, but not yet published: 0
d. • Number of books or chapters published (for each, provide a complete citation): 1
e. • Number of printed technical reports/non-refereed papers (for each, provide a complete citation: 0
f. • Number of patents filed: 3
g. • Number of patents granted (for each, provide a complete citation): 0
h. • Number of invited presentations (for each, provide a complete citation): 9
i. • Number of submitted presentations (for each, provide a complete citation): 2
j. • Honors/Awards/Prizes for contract/grant employees (list attached): 3
k. • Total number of Full-time Equivalent Graduate Students and Post-Doctoral associates supported during this period under PR project number: 4

Graduate Students:
Post-Doctoral Associates: 1

including the number of:
Female Graduate Students: 0
Female Post-Doctoral Associates: 0

the number of
Minority Graduate Students: 1
Minority Post-Doctoral Associates: 0

and the number of
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).

• Use the letter and an appropriate title as a heading for your list, e.g.:
b. Published Papers in Refereed Journals, or, d. Books and Chapters published.
Also submit the citation lists as ASCII files via email or via PC-compatible floppy disks.

• Minorities include Blacks, Aleuts, AmIndians, Hispanics, etc. NB: Asians are not considered an under-represented or minority group in science and engineering.

a. • Number of papers submitted to refereed journals, but not published: 3

1. P. Yang and C.M. Lieber, "Nanostructured high-temperature superconductors: creation of strong-pinning columnar defects in nanorod/superconductor composites", *J. Mater. Res.*, accepted for publication.

2. E.W. Wong, P.E. Sheehan and C.M. Lieber, "Nanobeam Mechanics: Elasticity, Strength and Toughness of Nanorods and Nanotubes", *Science*, submitted.

3. P. Yang and C.M. Lieber, "Nanostructured High-T_c Superconductors", *Chem. Mater.*, invited review.

b. • Number of papers published in refereed journals: 5

1. P. Yang and C.M. Lieber, "Nanorod-Superconductor Composites: A Pathway to High Critical Current Density Materials", *Science* **273**, 1836-1840 (1996).

2. H. Dai, E.W. Wong and C.M. Lieber, "Probing Electrical Transport in Nanomaterials: Conductivity of Individual Carbon Nanotubes", *Science* **272**, 523-526 (1996).

3. E.W. Wong, B.W. Maynor, L.D. Burns and C.M. Lieber, "Growth of Metal Carbide Nanotubes and Nanorods", *Chem. Mater.* **8**(8), 2041-2046 (1996).

4. P. Kim, Z. Yao, and C.M. Lieber, "Vortex Lattice Structure in $Bi_2Sr_2CaCu_2O_{8+d}$ at High Temperatures", *Phys. Rev. Lett.*, **77**(25) 5118-5121 (1996).

5. P. Yang and C.M. Lieber, "Columnar defect formation in nanorod/$Tl_2Ba_2Ca_2Cu_3O_z$ superconducting composites, *Appl. Phys. Lett.* **70**(23), 3158-3160 (1997).

d. • Number of books or chapters published (for each, provide a complete citation): 1

1. C.M. Lieber, A.M. Morales, P.E. Sheehan, E.W. Wong and P. Yang, "One-Dimensional Nanostructures: Rational Synthesis, Novel Properties and Applications", *in Proceedings of the Robert A. Welch Foundation 40th Conference on Chemical Research: Chemistry on the Nanometer Scale*, 165-187 (The Robert A. Welch Foundation: Houston, TX, 1997).

f. • Number of patents filed: 3

1. C.M. Lieber and P. Yang, "Metal Oxide Nanorods," 08/606,892, patent pending.

2. C.M. Lieber and E.W. Wong, "Preparation of Carbide Nanorods", patent pending.

3. C.M. Lieber and P. Yang, "Method of Producing Metal Oxide Nanorods", 08/790,824, patent pending.

h. • Number of invited presentations: 9

1. "Superconductivity Devices: New Advances Through Nanostructure Control", ONR/NSF Interfaces to Superconductors Mid-Term Review/Workshop, Buffalo, NY, June 1996.

2. "Nanomaterials: Present and Future Opportunities for Research and Technology", Defense Sciences Research Council's Workshop on Nanomaterials, La Jolla, CA, July 1996.

3. "Synthesis of Silicon Nanowires", Gordon Conference on Solid State Chemistry", New London, NH, July 1996.

4. "One-Dimensional Nanostructures: Rational Synthesis, Novel Properties and Applications", The Robert A. Welch Foundation 40th Conference on Chemical Research, Chemistry on the Nanometer Scale, Houston, TX, October 1996.

5. "Nanorod-Superconductor Composites for High Critical Current Densities", American Superconductor Corporation, Westborough, MA, October 1996.

6. "One-Dimensional Nanostructures: Rational Synthesis, Novel Properties and Applications", MRS Fall Meeting, Boston, MA, December 1996.

7. "1D Nanostructures: Rational Synthesis, Novel Properties and Applications", Department of Physics, Georgia Institute of Technology, Atlanta, GA, February 1997.

8. "Electrical and Mechanical Properties of Individual Nanotubes and Nanorods", APS Meeting, Kansas City, MO, March 1997.

9. "Carbon Nanotubes: Present and Future Opportunities", ONR-Rice University Workshop on Carbon Nanotubes - Opportunities, Requirement and Challenges, Houston, TX, May 1997.

i. • Number of submitted presentations: 2

1. "Nanostructured Superconductors", 213th National ACS Meeting, San Francisco, CA, April 1997.

2. "Rational Synthesis of Silicon Nanowires", 213th National ACS Meeting, San Francisco, CA, April 1997.

j. • Honors/Awards/Prizes for contract/grant employees: 3

1. 1996 Fellow of The American Physical Society

2. 1997 Fellow of The American Association for the Advancement of Science

3. Editorial Advisory Board, Chemistry of Materials, elected 1997.

1. • Other funding:

A. Agency: National Science Foundation
Grant Title: "Scanning Tunneling Microscopy Investigations of Low-Dimensional Materials."
Amount to be received this year: $150,000
Total Amount: $300,000
Period of Performance: 8/15/96 - 8/14/98

This grant has no direct overlap with the work of this ONR project.

B. Agency: Air Force Office of Scientific Research
Grant Title: "Nanotribology Investigations of Solid and Liquid Lubricants Using Scanned Probe Microscopies."
Amount received this year: $275,000
Total Amount: $575,000
Period of Performance: 11/1/96 - 10/31/99

This grant has no direct overlap with the work of this ONR project.

C. Agency: Air Force Office of Scientific Research
Grant Title: "Nanometric Studies of the Structure and Tribology of Carbon Nitride Materials."
Amount received this year: $275,000
Total Amount: $55,972
Period of Performance: 6/15/95 - 6/14/98

This grant has no direct overlap with the work of this ONR project.

D. Agency: Ballistic Missile Defense Organization
Grant Title: "Spectroscopic Characterization of Laser Ablation Plumes for Advanced Materials Growth."
Amount received this year: $150,900
Total Amount: $150,900
Period of Performance: 3/1/97 - 2/28/98

This grant has no direct overlap with the work of this ONR project.

E. Agency: National Science Foundation (Materials Research Science and Engineering Center)
Grant Title: "Long-Range Order and Winding of Vortices in High-T_c Superconductors"
P.I.s: D.R. Nelson and C.M. Lieber
Amount received this year: $50,000
Total Amount: $50,000
Period of Performance: 3/1/97 - 2/28/98

This grant has no direct overlap with the work of this ONR project.

F. Agency: National Science Foundation (Materials Research Science and Engineering Center)
Grant Title: "Synthesis of Superhard Carbon Nitride Materials"
P.I.s: C.B. Agee, M.J. Aziz and C.M. Lieber
Amount received this year: $50,000
Period of Performance: 3/1/97 - 2/28/98

This grant has no direct overlap with the work of this ONR project.

G. Agency: American Chemical Society - The Petroleum Research Fund
Grant Title: "Growth of 1-Dimensional Carbide Nanomaterials."
Amount received this year: $25,000
Total Amount: $50,000
Period of Performance: 1/1/97 - 8/31/99

This grant has no direct overlap with the work of this ONR project.

H. Agency: National Institutes of Health (subcontract from Brigham & Women's Hospital)
Grant Title: "Analysis of Alzheimer Amyloidogenesis with New Methods"
Amount received this year: $109,421
Total Amount: $109,421
Period of Performance: 6/1/97-5/30/98

This grant has no direct overlap with the work of this ONR project.

PART II

a. Principle Investigator: Charles M. Lieber

b. Current telephone number: (617) 496-3169

c. Cognizant ONR Scientific Officer: Dr. John C. Pazik

d. Program objective:

The overall goal of this project is to develop rational approaches for controlling the structure and interfaces of high-temperature superconductors (HTSs) and other complex solids at the nanometer scale. Our emphasis on nanometer scale is motivated by the recognition that control of structure in this size regime leads in general to materials with enhanced and/or novel electrical, mechanical, optical and magnetic properties. In this regard, our main objective has been to control the nanometer scale defect structure in HTSs since this will enable the intrinsic problem of thermally-activated flux flow, which limits critical currents in all HTS materials, to be significantly reduced. Specific objectives that have been pursued during the past year include (1) the design and synthesis of one-dimensional nanostructures (nanorods) that are chemically and structurally compatible with HTS materials, (2) the synthesis and structural characterization of nanorod/HTS nanocomposites, and (3) the elucidation of critical current behavior of nanorod/HTS materials as a function of temperature and magnetic field.

e. Significant results during last year:

A number of significant results have been obtained during the past year of this project, including: (1) the development of general synthetic methods to prepare new one-dimensional (1D) metal-oxide nanorods; (2) the successful preparation of MgO nanorod/HTS composites with HTS = $Bi_2Sr_2CaCu_2O_8$ (BSCCO-2212); (3) the discovery and elucidation of a novel self-organization process whereby MgO nanorods self-align in orientations perpendicular and parallel to the copper oxide planes; (4) the demonstration that MgO nanorod/BSCCO-2212 nanocomposites have critical current densities significantly larger at high temperatures and magnetic fields compared to conventional materials; and (5) the successful preparation of new MgO nanorod/HTS composites where HTS = $Tl_2Ba_2Ca_2Cu_3O_{10}$ and $Bi_2Sr_2Ca_2Cu_3O_{10}$. These results are making a significant impact in several ways. First, our proof-of-concept experiments with the MgO nanorod/BSCCO-2212 system have elicited significant interest by the major HTS wire manufacturers in the United States and Japan. Secondly, our demonstration of self-organization in this system has proven that our new approach can be applied to bulk materials. More generally, the approaches developed in this project are expected to impact efforts to create other nanostructured materials.

f. Brief summary of plans for next years work:

The major goals of this project for the coming year are as follows. We plan to develop significantly the synthesis and understanding of bulk nanorod/BSCCO materials (2212 and 2223), since these systems may have the largest impact on technology. Effort will be placed on characterizing and optimizing nanostructure in these materials, as well as, on making and characterizing the transport critical current behavior in small wire structures. We also plan to pursue the fabrication of ordered arrays of nanorods on substrates (for both HTS and other applications), and to develop further and explore the new concepts of nanorod growth and self-organized nanostructured materials that are emerging from this project.

g. List of names of graduate students and post-doctoral(s) currently working on project:

1. Peidong Yang
2. Christian Bolle (postdoctoral associate)
3. Eric Wong
4. Qingqiao Wei

Part III

Principle Investigator: Charles M. Lieber

Project Title: "Organized Nanorod-Superconductor Composites"

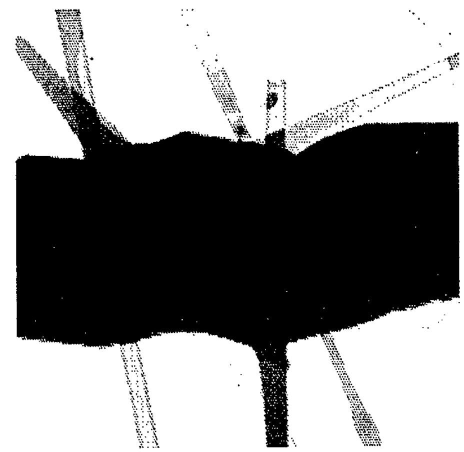
Cognizant ONR Scientific Officer: Dr. John C. Pazik

Highlights of Research Project: 6/96 - 6/97

Nanostructured High Temperature Superconductors

Technology Issues: the critical current density impacts all HTS application areas: power transmission; motors; magnets; communications; sensors. key issues are HTS structure and defects

Objectives: prepare 1-dimensional (1D) nanorods; prepare & characterize nanorod/HTS composites; demonstrate as method for enhanced critical currents



Approach:

- create nanostructured HTS materials with columnar defect structure
- use chemically compatible 1D nanorods within HTS matrix

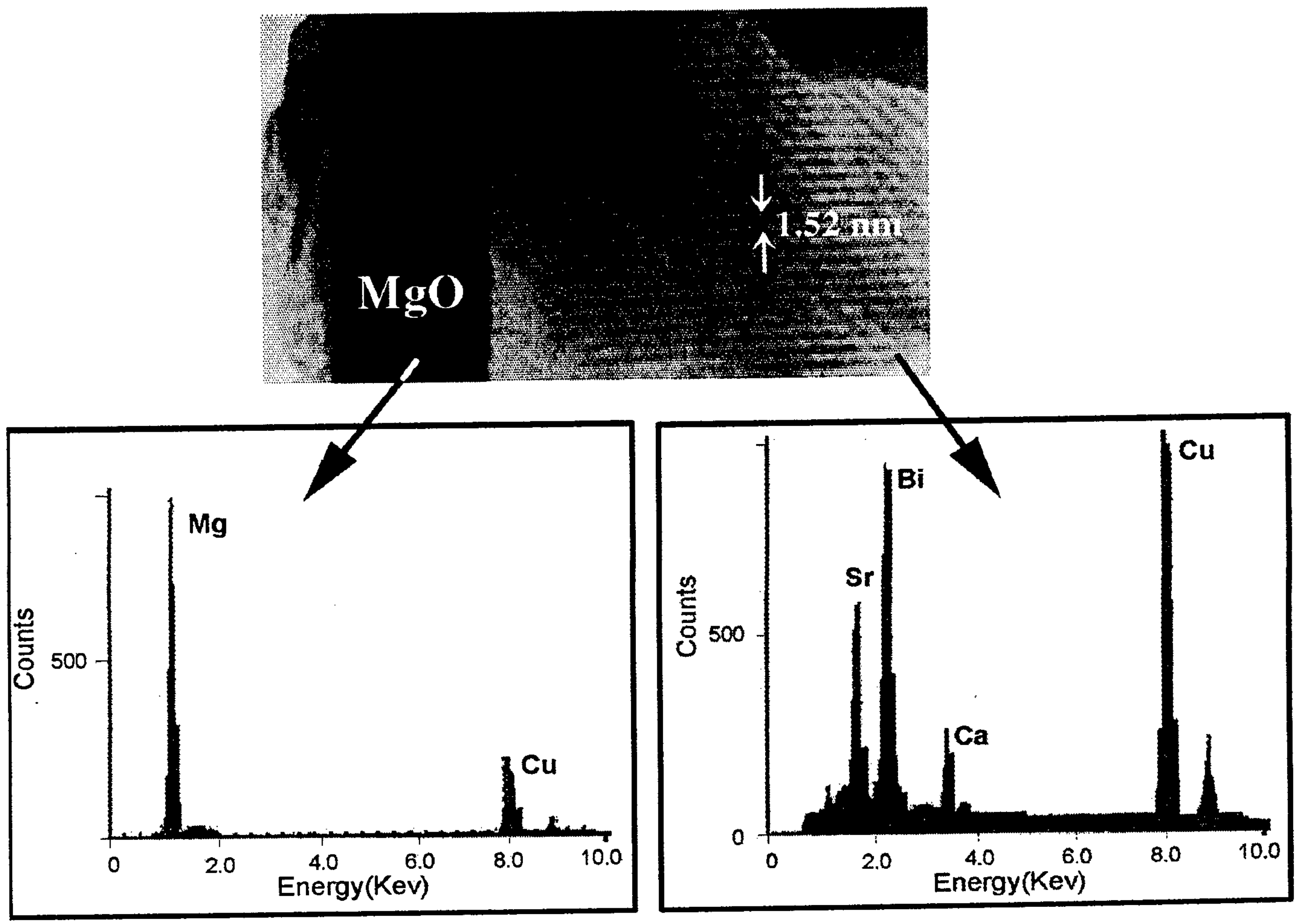
Accomplishments:

- MgO nanorods with required structure, chemical reactivity and anisotropy synthesized
- nanorod/HTS superconductor bulk and film composites prepared and shown to have columnar defects structure
- nanorod/HTS materials with enhanced critical currents demonstrated

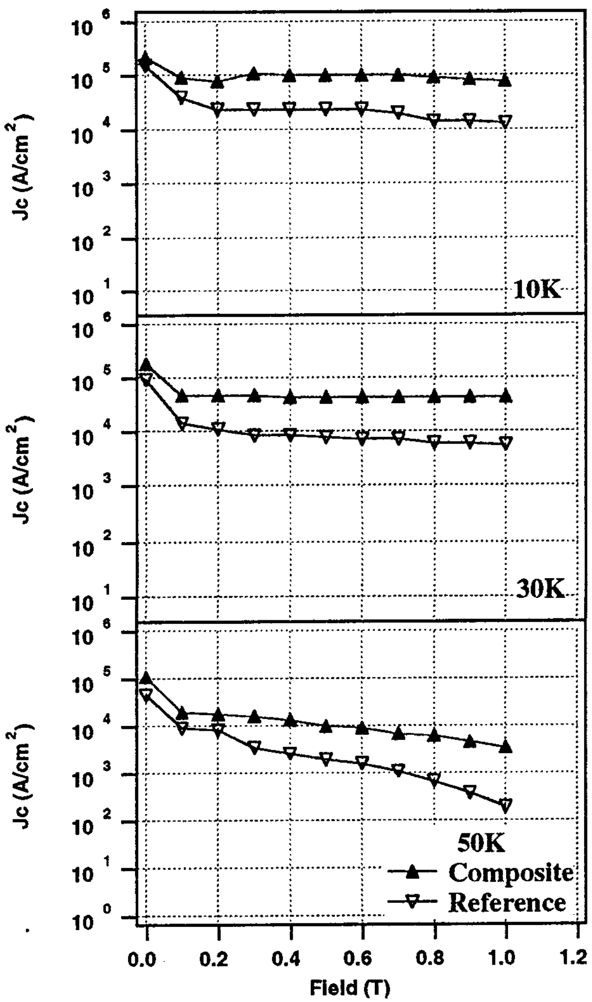
Impact & Transition

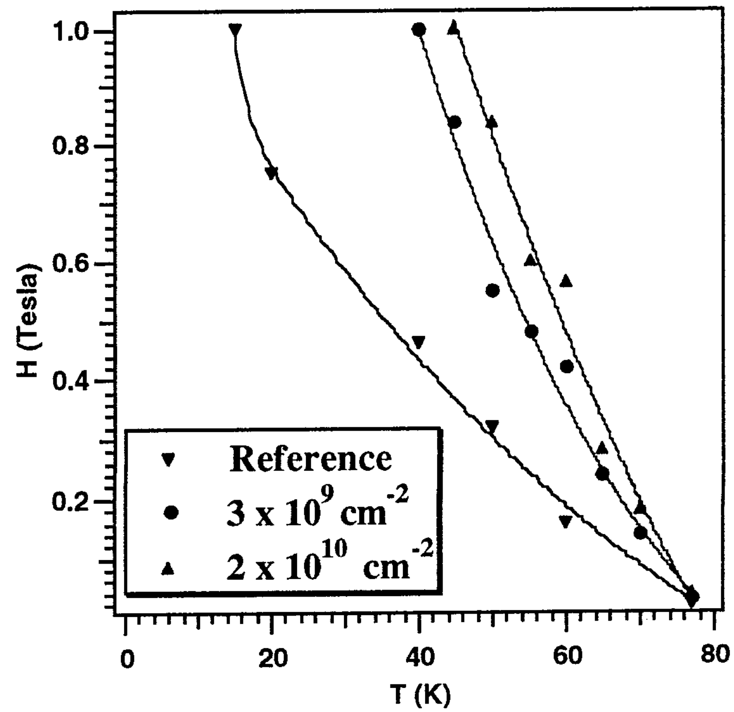
- nanorod/HTS S&T being explored for large scale power cables (American Superconductor Corp. & Sumitomo)
- patterned nanorod/HTS films being explored for low-noise SQUID detectors (Quantum Magnetics)
- new and general approach for nanostructured materials

MgO Nanorod/HTS Interface



Nanorod/BSCCO Transport Properties





Description of Viewgraphs.

1. Transmission electron microscopy image of a MgO nanorod/$Bi_2Sr_2CaCu_2O_8$ (BSCCO-2212) composite. In this image, a large number of MgO nanorods penetrate through a BSCCO-2212 crystal grain (black) approximately perpendicular to the copper oxide planes. These nanorods create a columnar defect structure that is ideal for pinning magnetic vortices and thereby enhancing critical currents.

2. High-resolution transmission electron microscopy image (top center) of a single MgO nanorod within BSCCO-2212. The sample was obtained from a bulk composite. The MgO nanorod appears black in this image and the BSCCO-2212 image gray. The image shows clearly the layered structure of the BSCCO-2212 matrix (**c**/2=1.52 nm) with the nanorod oriented perpendicular to the layers. The image also demonstrates that MgO nanorods form a structurally sharp interface with the HTS matrix. Element sensitive EDAX spectra (lower left/right) recorded across the nanorod/BSCCO-2212 interface using a 10 nm electron beam diameter also demonstrate that this interface is compositionally sharp; that is, no Mg signal is detected after moving several nanometers beyond location of the MgO nanorod.

3. (left) Comparisons of the critical current density (J_c) as a function of magnetic field determined at three distinct temperatures for nanorod/BSCCO-2212 composite and BSCCO-2212 reference samples. The critical current densities were determined from current-voltage curves on half centimeter length HTS-Ag tapes, and thus correspond to a good representation of the behavior that can be expected in current carrying wires. The nanorod/BSCCO-2212 composites exhibit 10x improvements in J_c in the technologically relevant high temperature and field regime. (right) Plots of the irreversibility lines for nanorod/BSCCO-2212 and BSCCO-2212 samples. The composite samples contain an in-plane density of nanorods of either 3 x $10^9/cm^2$ or 2 x $10^{10}/cm^2$. The irreversibility line defines the region below which the superconductor can be operated without loss (as a true superconductor). This plot shows that the operating regime of the composites is extended significantly, since the irreversibility lines of these materials are shifted upwards.