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26-10-2012	Final Report	27-Sep-2007 - 31-Jul-2012

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Final Technical Report: Chemical Communications

5a. CONTRACT NUMBER
W911NF-07-1-0618

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
7620AK

6. AUTHORS
Fiorenzo G. Omenetto, David L. Kaplan

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES
Tufts University
Office of the Vice Provost
Tufts University
Medford, MA 02155 -5807

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
U.S. Army Research Office
P.O. Box 12211
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53392-MS-DRP.47

12. DISTRIBUTION AVAILABILITY STATEMENT
Approved for Public Release; Distribution Unlimited

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The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT
Significant progress was achieved throughout this project. The automatization of silk solution was developed. Examination of different processing conditions for the raw material showed promise for higher durability and higher flexibility optical substrates. Progress on interfaces was solidified. The previous findings on silk-metal interfaces were successfully exploited for the development of structures for use in integrated silk protein devices. We succeeded in demonstrating parallel transfer on microstructured gold structures onto silk films for large-area

15. SUBJECT TERMS
biomaterials processing, silk interfaces, fabrication, devices, optical components

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			David Kaplan
UU	UU	UU	UU		19b. TELEPHONE NUMBER 617-627-3251

Standard Form 298 (Rev 8/98)
Prescribed by ANSI Std. Z39.18

Report Title

Final Technical Report: Chemical Communications

ABSTRACT

Significant progress was achieved throughout this project. The automatization of silk solution was developed. Examination of different processing conditions for the raw material showed promise for higher durability and higher flexibility optical substrates. Progress on interfaces was solidified. The previous findings on silk-metal interfaces were successfully exploited for the development of structures for use in integrated silk protein devices. We succeeded in demonstrating parallel transfer on microstructured gold structures onto silk films for large-area manufacturing of micro- and nanoscale structures. Demonstration of a combination of structural color imprinting on doped (fluorescent) films was pursued for structure-dependent fluorescence enhancement. We also demonstrated the first use of silk as a gate dielectric in an organic semiconductor device and a variety of metamaterial structures. The latter function as environmental sensors by wirelessly transducing environmental perturbations. In addition, the direct inclusion of dopants or the use of surface chemistries to add function to silk, were successful directions pursued. Among the most interesting modifications of silk were the explorations of silk solution doped with Au-nanoparticles (NP). This silk can be transformed in multiple material formats maintaining a high concentration of Au-NP without aggregation, and allowing for thermal management of the film via optical excitation.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Silk photonics, UC Irvine (2011)
Silk – the ancient material of the future, TED, Long Beach, CA (2011)
Flex Electronics, Lemelson Prize Colloquium, MIT (2011)
Silk Photonics, New York Academy of Sciences (2011)
Silk Technology – Plenary talk at Singapore ICYRAM-MRS (2012)
Inspiring Matter – Royal College of Art London (2012)
Silk Workshop, France, DoD sponsored (2012)

Number of Presentations: 7.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received	Paper

07/23/2008 1.00 S.T. Parker, P. Domachuk, J. Amsden, J. Bressner, J.A. Lewis, D.L. Kaplan, F.G. Omenetto. Biocompatible Silk Printed Optical Waveguides,
( )

07/23/2008 2.00 P. domachuk, H. Perry, D.L. Kaplan, F. Omenetto. Bioactive Optofluidic Devices,
( )

09/14/2011 5.00 Hu Tao, Andrew Strikwerda, Mengkun Liu, Jessica Mondia, Evren Ekmekci, Kebin Fan, David Kaplan, Willie Padilla, Xin Zhang, Richard Averitt, Fiorenzo Omenetto. Performance enhancement of terahertz metamaterials on ultrathin substrates for sensing applications ,
Applied Physics Letters (12 2010)

09/14/2011 20.00 Carlo Forestiere, Massimo Donelli, Gary Walsh, Edoardo Zeni, Giovanni Miano, Luca Dal Negro. Particle swarm optimization of broadband nanoplasmonic arrays,
Optics Letters (01 2010)

09/14/2011 19.00 R Capelli, Jason Amsden, G Generali, S Toffanin, V Benfenati, M Muccini, David Kaplan, Fiorenzo Omenetto, Roberto Zamboni. Integration of silk protein in organic and light emitting transistors,
Organic Electronics (04 2011)

09/14/2011 18.00 Konstantinos Tsioris, Hu Tao, Mengkum Liu, Jeffrey Hopwood, David Kaplan, Richard Averitt, Fiorenzo Omenetto. Rapid transfer-based micro patterning and dry etching of silk microstructures,
Advanced Materials (03 2011)

09/14/2011 16.00 Lindsay Wray, Xiao Hu, Daniel Schmidt, Jabier Gallego, Irene Georgakoudi, Fiorenzo Omenetto, David Kaplan. Effect of Processing on Silk-Based Biomaterials: Reproducibility and Biocompatibility,
Journal of Biomedical Materials Research Part B: Applied Biomaterials (03 2011)

09/14/2011 15.00 Hu Tao, Logan Chieffo, Mark Brenkle, Sean Siebert, Andrew Strikwerda, Kebin Fan, David Kaplan, Xin Zhang, Richard Averitt, Fiorenzo Omenetto. Metamaterials on Paper as a Sensing Platform,
Advanced Materials (06 2011)

09/14/2011 14.00 Dae-Hyeong Kim, Nanshu Lu, Rui Ma, Yun-Soung Kim, Rak-Hwan Kim, Shuodao Wang, Jian Wu, Sang Min Won, Hu Tao, Ahmad Islam, Ki Jun Yu, Tae-il Kim, Raeed Chowdhury, Ming Ying, Lizhi Xu, Ming Li, Hyun-Joong Chung, Hohyun Keum, Martin McCormick, Ping Liu, Yong-Wei Zhang, Fiorenzo Omenetto, Yonggang Huang, Todd Coleman, John Rogers. Epidermal Electronics,
Science (08 2011)

09/14/2011 13.00 Svetlana Boriskina, Sylvanus Lee, Jason Amsden, Fiorenzo Omenetto, Luca Dal Negro. Formation of Colorimetric Fingerprints on Nano-Patterned Deterministic Aperiodic Surfaces,
Optics Express (06 2010)

09/14/2011 12.00 Sylvanus Y Lee, Jason Amsden, Svetlana Boriskina, Ashwin Gopinath, Alexander Mitropolous, David Kaplan, Fiorenzo Omenetto, Luca Dal Negro. Spatial and Spectral Detection of Protein Monolayers with Deterministic Aperiodic Arrays of Metal Nanoparticles,
Proceedings of the National Academy of Sciences(US) (07 2010)

09/14/2011 10.00 Fiorenzo Omenetto, David Kaplan. New Opportunities for an Ancient Material,
Science (09 2011)

09/14/2011 9.00 RH Kim, DH Kim, J Xiao, B Hoon Kim, S Park, Bruce Panilaitis, R Ghaffari, J Yao, M Li, Z Liu, V Malyarchuk, DG Kim, A Le, Ralph Nuzzo, David Kaplan, Fiorenzo Omenetto, Y Huang, Z Kang, John Rogers. Waterproof AlInGaP Optoelectronics on Flexible Tubing, Sutures, Gloves and Other Unusual Substrates, With Application Examples in Biomedicine and Robotics,
Nature Materials (10 2010)

09/14/2011	8.00	Hu Tao, Sean Siebert, Mark Brenckle, Richard Averitt, Mark Cronin-Golomb, David Kaplan, Fiorenzo Omenetto. Gold Nanoparticle-Doped Biocompatible Silk Films as a Path to Implantable Thermal-electrically Wireless Powering Devices, Applied Physics Letters (09 2010)
09/14/2011	7.00	Jessica Mondia, Jason Amsden, D Lin, Luca Dal Negro, David Kaplan, Fiorenzo Omenetto. Rapid Nanoimprinting of Doped Silk Films for Enhanced Fluorescent Emission, Advanced Materials (09 2010)
09/14/2011	6.00	Fiorenzo Omenetto, David Kaplan. From silk cocoon to medical miracle, Scientific American (09 2011)
09/15/2009	4.00	D. Kaplan, F. Omenetto, M. Zakin, J. Rogers, D. Kim, Y. Kim, J. Amsden, B. Panilaitis. Silicon Electronics on Silk as a Path to Bioresorbable, Implantable Devices, ( )
11/17/2008	3.00	Brian D. Lawrence, Fiorenzo Omenetto, David L. Kaplan. Processing Methods to Control Silk Fibroin Film Biomaterial Features, Journal of Materials Science ( )

TOTAL: **18**

Number of Manuscripts:

Books

Received Paper

TOTAL:

Patents Submitted

Edible holographic silk products
~~Nanoimprinting of silk fibroin films for biomedical and optical device applications~~
Silk room-temperature, low-pressure nanoimprinting
Immobilization and storage of penicillin
Silk metamaterials
Silk reflectors
Visible light structural color-based sensing of monolayers of protein in the visible regime
Blue silk laser
Silk organic FET (silk as a dielectric on organic transistor devices)
Waterproof AlInGaP Optoelectronics on Catheter Balloons, Structures, Gloves and Other Unusual Substrates, with Applications in Biomedicine and Robotics
Silk fibroin systems for antibiotic activity
Nanoparticle doped silk materials
Method for making silk inverse opal structure
Silk-based conformal, adhesive, edible sensors

Patents Awarded

Awards

Fio Omenetto – Guggenheim Fellow 2011, NSF INSPIRE Award
Fio Omenetto – Fellow Optical Society of America 2012
John Rogers - 2011 MIT Lemelson Prize

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
Konstantinos Tsioris	1.00	
Alexander Mitropolous	1.00	
Mark Paquette	1.00	
Benjamin Partlow	1.00	
Sylvanus Lee	1.00	
Daimin Lin	0.00	
Jason Bressner	1.00	
Yuji Zhang	1.00	
Tae Il Kim	0.75	
FTE Equivalent:	**7.75**	
Total Number:	**9**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
Svetlana Boriskina	0.40
Hu Tao	1.00
Sunghwan Kim	1.00
Suk Won Hong	0.25
Jong Ho Lee	0.10
Reza Saeidpourazar	0.60
Byung Duk Yang	0.40
Xiao Hu	0.50
Waseem Raja	0.50
FTE Equivalent:	**4.75**
Total Number:	**9**

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
David Kaplan	0.10	No
Fiorenzo Omenetto	0.15	
Bruce Panilaitis	0.10	
Gary Leisk	0.05	
FTE Equivalent:	**0.40**	
Total Number:	**4**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED	Discipline
Lauren Klinker	0.10	Biomedical Engineering
Mark Brenckle	0.10	Biomedical Engineering
Eric Takasugi	0.10	Physics
Ryan Orendorff	0.10	Biomedical Engineering
FTE Equivalent:	**0.40**	
Total Number:	**4**	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period:	2.00
The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:......	2.00
The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:......	2.00
Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):......	1.00
Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:......	0.00
The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense	0.00
The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:......	0.00

Names of Personnel receiving masters degrees

NAME	
Jason Bressner	
Benjamin Partlow	
Dainmin Lin	
Total Number:	**3**

Names of personnel receiving PHDs

NAME	
Konstantinos Tsioris	
Total Number:	**1**

Names of other research staff

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

1 a. Boston University	1 b. Office of Sponsored Programs			
	Trustees of Boston University			
	Boston	MA	02215	
Sub Contractor Numbers (c):				
Patent Clause Number (d-1):				
Patent Date (d-2):				
Work Description (e):				
Sub Contract Award Date (f-1):				
Sub Contract Est Completion Date(f-2):				

1 a. Boston University	1 b. 881 Commonwealth Avenue		
	Boston	MA	022151303
Sub Contractor Numbers (c):			
Patent Clause Number (d-1):			
Patent Date (d-2):			
Work Description (e):			
Sub Contract Award Date (f-1):			
Sub Contract Est Completion Date(f-2):			

1 a. University of Illinois - Urbana - Champaign	1 b. BOARD OF TRUSTEES OF THE UNIV		
	1901 S. First Street, Suite A		
	Champaign	IL	618207406
Sub Contractor Numbers (c):			
Patent Clause Number (d-1):			
Patent Date (d-2):			
Work Description (e):			
Sub Contract Award Date (f-1):			
Sub Contract Est Completion Date(f-2):			

1 a. University of Illinois - Urbana - Champaign	1 b. Grants & Contracts Office		
	Office of Business & Financial Services		
	Champaign	IL	618207406
Sub Contractor Numbers (c):			
Patent Clause Number (d-1):			
Patent Date (d-2):			
Work Description (e):			
Sub Contract Award Date (f-1):			
Sub Contract Est Completion Date(f-2):			

Inventions (DD882)

5 **Blue silk lasers**

Patent Filed in US? (5d-1) Y

Patent Filed in Foreign Countries? (5d-2) N

Was the assignment forwarded to the contracting officer? (5e) N

Foreign Countries of application (5g-2):

5a: David L. Kaplan

5f-1a: Tufts University

5f-c: 4 Colby Street

Medford MA 02155

5a: Jason Amsden

5f-1a: Tufts University

5f-c: 4 Colby Street

Medford MA 02155

5a: Fiorenzo G Omenetto

5f-1a: Tufts University

5f-c: 4 Colby Street

Medford MA 02155

5a: Catherine Kitts

5f-1a:

5f-c:

5a: Michele Muccini

5f-1a: CNR Bologna

5f-c:

5a: Stefano Toffanin

5f-1a: CNR Bologna

5f-c:

5a: Roberto Zamboni

5f-1a: CNR Bologna

5f-c:

5 **Eidble holographic silk products**

Patent Filed in US? (5d-1) Y

Patent Filed in Foreign Countries? (5d-2) N

Was the assignment forwarded to the contracting officer? (5e) N

Foreign Countries of application (5g-2):

5a: David L Kaplan

5f-1a: Tufts University
5f-c: 4 Colby Street
Medford MA 02155

5a: Fiorenzo G Omenetto

5f-1a: Tufts University
5f-c: 4 Colby Street
Medford MA 02155

5 **Immobilization and storage of penicillin**

Patent Filed in US? (5d-1) Y
Patent Filed in Foreign Countries? (5d-2) N
Was the assignment forwarded to the contracting officer? (5e) N
Foreign Countries of application (5g-2):

5a: Fiorenzo G Omenetto

5f-1a: Tufts University
5f-c: 4 Colby Street
Medford MA 02155

5a: Eleanor Pritchard

5f-1a: Tufts University
5f-c: 4 Colby Street
Medford MA 02155

5a: David L. Kaplan

5f-1a: Tufts University
5f-c: 4 Colby Street
Medford MA 02155

5 **Method for making silk inverse opal structure**

Patent Filed in US? (5d-1) Y
Patent Filed in Foreign Countries? (5d-2) N
Was the assignment forwarded to the contracting officer? (5e) N
Foreign Countries of application (5g-2):

5a: Fiorenzo G Omenetto

5f-1a: Tufts University
5f-c: 4 Colby Street
Medford MA 02155

5a: Sunghwan Kim

5f-1a: Tufts University
5f-c: 4 Colby Street
Medford MA 02155

5a: David L. Kaplan

5f-1a: Tufts University

5f-c: 4 Colby Street

Medford MA 02155

5 **Nanoimprinting of silk fibroin films for biomedical and optical device**

Patent Filed in US? (5d-1) Y

Patent Filed in Foreign Countries? (5d-2) N

Was the assignment forwarded to the contracting officer? (5e) N

Foreign Countries of application (5g-2):

5a: Fiorenzo G Omenetto

5f-1a: Tufts University

5f-c: 4 Colby Street

Medford MA 02155

5a: David L Kaplan

5f-1a: Tufts University

5f-c: 4 Colby Street

Medford MA 02155

5a: Jason J Amsden

5f-1a: Tufts University

5f-c: 4 Colby Street

Medford MA 02155

5 **Nanoparticle doped silk materials**

Patent Filed in US? (5d-1) Y

Patent Filed in Foreign Countries? (5d-2) N

Was the assignment forwarded to the contracting officer? (5e) N

Foreign Countries of application (5g-2):

5a: Fiorenzo G Omenetto

5f-1a: Tufts University

5f-c: 4 Colby Street

Medford MA 02155

5a: David L. Kaplan

5f-1a: Tufts University

5f-c: 4 Colby Street

Medford MA 02155

5a: Hu Tao

5f-1a: Tufts University

5f-c: 4 Colby Street

Medford MA 02155

5 **Silk fibroin systems for antibiotic activity**

Patent Filed in US? (5d-1) Y

Patent Filed in Foreign Countries? (5d-2) N

Was the assignment forwarded to the contracting officer? (5e) N

Foreign Countries of application (5g-2):

5a: Eleanor Pritchard

5f-1a: Tufts University

5f-c: 4 Colby Street

Medford MA 02155

5a: Fiorenzo G Omenetto

5f-1a: Tufts University

5f-c: 4 Colby Street

Medford MA 02155

5a: Bruce Panilaitis

5f-1a: Tufts University

5f-c: 4 Colby Street

Medford MA 02155

5a: David L. Kaplan

5f-1a: Tufts University

5f-c: 4 Colby Street

Medford MA 02155

5 **Silk metamaterials**

Patent Filed in US? (5d-1) Y

Patent Filed in Foreign Countries? (5d-2) N

Was the assignment forwarded to the contracting officer? (5e) N

Foreign Countries of application (5g-2):

5a: Fiorenzo G Omenetto

5f-1a: Tufts University

5f-c: 4 Colby Street

Medford MA 02155

5a: Jason Amsden

5f-1a: Tufts University

5f-c: 4 Colby Street

Medford MA 02155

5a: Hu Tao

5f-1a: Tufts University

5f-c: 4 Colby Street

Medford MA 02155

5a: Richard Averitt

5f-1a: Boston University

5f-c: 590 Commonwealth Ave

Boston MA 02215

5a: Andrew Strikewerda

5f-1a: Boston University

5f-c: 590 Commonwealth Ave

Boston MA 02215

5a: David L Kaplan

5f-1a: Tufts University

5f-c: 4 Colby Street

Medford MA 02155

5a: Xin Zhang

5f-1a: Boston University

5f-c: 110 Cummington St

Boston MA 02215

5 **Silk organic FET (silk as a dielectric on organic transistor devices)**

Patent Filed in US? (5d-1) Y

Patent Filed in Foreign Countries? (5d-2) N

Was the assignment forwarded to the contracting officer? (5e) N

Foreign Countries of application (5g-2):

5a: Jason Amsden

5f-1a: Tufts University

5f-c: 4 Colby Street

Medford MA 02155

5a: David L. Kaplan

5f-1a: Tufts University

5f-c: 4 Colby Street

Medford MA 02155

5a: Stefano Toffanin

5f-1a: CNR Bologna

5f-c:

5a: Roberto Zamboni

5f-1a: CNR Bologna

5f-c:

5a: Raffaella Capelli

5f-1a: CNR Bologna

5f-c:

5a: Michele Muccini

5f-1a: CNR Bologna

5f-c:

5a: Fiorenzo G Omenetto

5f-1a: Tufts University

5f-c: 4 Colby Street

Medford MA 02155

5 **Silk reflectors**

Patent Filed in US? (5d-1) Y

Patent Filed in Foreign Countries? (5d-2) N

Was the assignment forwarded to the contracting officer? (5e) N

Foreign Countries of application (5g-2):

5a: David L. Kaplan

5f-1a: Tufts University

5f-c: 4 Colby Street

Medford MA 02155

5a: Fiorenzo G Omenetto

5f-1a: Tufts University

5f-c: 4 Colby Street

Medford MA 02155

5 **Silk room-temperature, low-pressure nanoimprinting**

Patent Filed in US? (5d-1) Y

Patent Filed in Foreign Countries? (5d-2) N

Was the assignment forwarded to the contracting officer? (5e) N

Foreign Countries of application (5g-2):

5a: Fiorenzo G Omenetto

5f-1a: Tufts University

5f-c: 4 Colby Street

Medford MA 02155

5a: Jason J Amsden

5f-1a: Tufts University

5f-c: 4 Colby Street

Medford MA 02155

5a: David L Kaplan

5f-1a: Tufts University

5f-c: 4 Colby Street

Medford MA 02155

5 **Silk-based conformal, adhesive, edible sensors**

Patent Filed in US? (5d-1) Y

Patent Filed in Foreign Countries? (5d-2) N

Was the assignment forwarded to the contracting officer? (5e) N

Foreign Countries of application (5g-2):

5a: Hu Tao

5f-1a: Tufts University

5f-c: 4 Colby Street

Medford MA 02155

5a: David L Kaplan

5f-1a: Tufts University

5f-c: 4 Colby Street

Medford MA 02155

5a: Fiorenzo G Omenetto

5f-1a: Tufts University

5f-c: 4 Colby Street

Medford MA 02155

5 **Visible light structural color-based sensing of monolayers of protein in the visible regime**

Patent Filed in US? (5d-1) Y

Patent Filed in Foreign Countries? (5d-2) N

Was the assignment forwarded to the contracting officer? (5e) N

Foreign Countries of application (5g-2):

5a: Fiorenzo G Omenetto

5f-1a: Tufts University

5f-c: 4 Colby Street

Medford MA 02155

5a: Luca Dal Negro

5f-1a: Boston University

5f-c: 590 Commonwealth Ave

Boston MA 02215

5a: Jason Amsden

5f-1a: Tufts University

5f-c: 4 Colby Street

Medford MA 02155

5a: David L. Kaplan

5f-1a: Tufts University

5f-c: 4 Colby Street

Medford MA 02155

5 **Waterproof AlInGaP Optoelectronics on Catheter Balloons, Structures, Gloves and Other Unusual Substrates, with Applications in Biomec**

Patent Filed in US? (5d-1) Y

Patent Filed in Foreign Countries? (5d-2) N

Was the assignment forwarded to the contracting officer? (5e) N

Foreign Countries of application (5g-2):

5a: John A rogers

5f-1a: University of Illinois

5f-c: Room 308, 1304 W. Green St.

Urbana IL 61801

5a: Dae-Hyeong Kim

5f-1a: University of Illinois

5f-c: Room 308, 1304 W. Green St.

Urbana IL 61801

5a: Rak Hwan Kim

5f-1a: University of Illinois

5f-c: 1304 W. Green St.

Urbana IL 61801

Scientific Progress

See Attachment

Technology Transfer

FINAL PROGRESS REPORT
September 27, 2007- July 31, 2012

(1) Submissions or publications under ARO sponsorship during this reporting period. List the title of each and give the total number for each of the following categories

(a) Papers published in peer-reviewed journals 26

(b) Papers published in non-peer-reviewed journals 0

(c) Presentations 7

i. Presentations at meetings, but not published in Conference Proceedings 7

ii. Non-Peer-Reviewed Conference Proceeding publications (other than abstracts) 0

iii. Peer-Reviewed Conference Proceeding publications (other than abstracts) 0

(d) Manuscripts 0

(e) Books 0

(f) Honors and Awards

Fio Omenetto – Guggenheim Fellow 2011, NSF INSPIRE Award

Fio Omenetto – Fellow Optical Society of America 2012

John Rogers – 2011 MIT Lemelson Prize

(g) Title of Patents Disclosed during the reporting period

Edible holographic silk products

Nanoimprinting of silk fibroin films for biomedical and optical device applications

Silk room-temperature, low-pressure nanoimprinting

Immobilization and storage of penicillin

Silk metamaterials

Silk reflectors

Visible light structural color-based sensing of monolayers of protein in the visible regime

Blue silk laser

Silk organic FET (silk as a dielectric on organic transistor devices)

Waterproof AlInGaP Optoelectronics on Catheter Balloons, Structures, Gloves and Other Unusual Substrates, with Applications in Biomedicine and Robotics

Silk fibroin systems for antibiotic activity

Nanoparticle doped silk materials

Method for making silk inverse opal structure

Silk-based conformal, adhesive, edible sensors

(h) Patents Awarded during the reporting period NA

(2) Student/Supported Personnel Metrics for this Reporting Period (name, % supported, %Full Time Equivalent (FTE) support provided by this agreement, and total for each category)

(a) Graduate Students 8

Konstantinos Tsioris, Tufts University, (100%, 1.0 FTE)

Alexander Mitropoulos, Tufts University, (100%, 1.0)

Mark Paquette, Tufts University, (100%, 1.0)

Benjamin Partlow, Tufts University, (100%, 1.0)

Sylvanus Lee, Boston University, (100%, 1.0)

Dainmin Lin, Boston University, (100%, 1.0)

Jason Bressner, Tufts University, (100%, 1.0) (end with MS, June 2011)

Yuji Zhang, Tufts University, (100%, 1.0)

Tae Il Kim, UIUC, (75%, 0.75)

(b) Post Doctorates 8

Svetlana Boriskina, Boston University, (40%, 0.4)

Hu Tao, Tufts University, (100%, 1.0)

Sunghwan Kim, Tufts University, (100%, 1.0)

Suk Won Hong, UIUC, (25%, 0.25)

Jong Ho Lee, UIUC, (10%, 0.1)

Reza Saeidpourazar, UIUC, (60%, 0.6)

Byung Duk Yang, UIUC, (40%, 0.4)

Xiao Hu, Tufts University, (50%, 0.5)

Waseem Raja, Tufts University, (50%, 0.5)

(c) Faculty 4

Prof. Fiorenzo Omenetto, Tufts University, 2 month summer salary (0.2 FTE)

Prof. David Kaplan, Tufts University, 1 month summer salary (0.1 FTE)

Prof. Luca Dal Negro, Boston University, 1 month of summer salary (0.05 FTE)

Prof. John A. Rogers, University of Illinois

(d) Undergraduate Students 4

Lauren Klinker, Tufts University

Mark Brenckle, Tufts University (now grad student)

Eric Takasugi, Tufts University

Ryan Orendorff, Tufts University

(e) Graduating Undergraduate Metrics (funded by this agreement and graduating during this reporting period):

Mark Brenckle

i. Number who graduated during this period 2

Mark Brenckle, BS BME

Ryan Orendorff, BS BME

ii. Number who graduated during this period with a degree in science, mathematics, engineering, or technology fields 2

Mark Brenckle, BS BME

Ryan Orendorff, BS BME

iii. Number who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields 2

Mark Brenckle, BS BME, now pursuing a PhD in BME at Tufts

Ryan Orendorff, BS BME, now pursuing a PhD in BME at UC-Berkeley

iv. Number who achieved a 3.5 GPA to 4.0 (4.0 max scale) 1

v. Number funded by a DoD funded Center of Excellence grant for Education, Research and Engineering unknown

vi. Number who intend to work for the Department of Defense unknown

vii. Number who will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields 1

(f) Masters Degrees Awarded (Name of each, Total #) 3

Jason Bressner, Tufts University, MS Biomedical Engineering, May 2010

Benjamin Partlow, Tufts University, MS Mechanical Engineering, May 2012

Dainmin Lin, Boston University, MS Electrical & Computer Engineering, May 2012

(g) Ph.D.s Awarded (Name of each, Total #) 1

Konstantinos Tsioris, May, 2012

(h) Other Research staff (Name of each, FTE % Supported for each, Total % Supported)

Research Faculty:

Prof. Gary Leisk, Tufts University, 1 month salary

Prof. Bruce Panilaitis, Tufts University, 3 months salary

(3) "Technology transfer" (any specific interactions or developments which would constitute technology transfer of the research results). Examples include patents, initiation of a start-up company based on research results, interactions with industry/Army R&D Laboratories or transfer of information which might impact the development of products.

Collaborations ongoing with Air Force Research Labs in Dayton, Ohio to use silk as a substrate for anti-tampering devices and for structural color. Additional collaboration initiated with Princeton University (Michael McAlpine), UCSD (Mauricio Montal), MIT (Michael Strano, Ed Boyden).

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(4) Scientific Progress and Accomplishments (description should include significant theoretical or experimental advances)

The scientific progress to date is summarized below:

Biomaterials processing –

The automatization of silk solution was developed. Examination of different processing conditions for the raw material showed promise for higher durability and higher flexibility optical substrates. There are still multiple sources (Japanese cocoons, Cambodian cocoons, Taiwanese cocoons, Chinese cocoons, Indian cocoons, raw silk textile fibers) being examined for material supplies including different extraction and purification steps.

- An automatized system for silk solution production was put in place in a new dedicated laboratory. This includes a custom-built extraction machine for raw material preparation, and an automated milli-Q water exchange station for parallel dialysis of the silk solution. The rate of silk solution production is now increased 6-10 fold.

- Solution repeatability remains a challenge and requires attention to detail. Through established QC steps we have identified optimum parameters for the preparation of materials for optical devices to specific solubilization parameters and raw material sources.

- The overall process is now ready for commercialization, for example, to establish a scale up facility and overall QA/QC requirements.

Silk interfaces - Progress on interfaces was solidified. The previous results and findings on silk-metal interfaces were successfully exploited for the development of structures for use in integrated silk protein devices. We have succeeded in demonstrating parallel transfer on microstructured gold structures onto silk films for large-area manufacturing of micro- and nanoscale structures. Additional demonstration of a combination of structural color imprinting on doped (fluorescent) films was pursued for structure-dependent fluorescence enhancement. We have also demonstrated the first use of silk as a gate dielectric in an organic semiconductor device and a variety of metamaterial structures. The latter function as environmental sensors by wirelessly transducing environmental perturbations. Additionally, we are explored the silk-Au interface to deposit inductive coils on the surface of the devices for wirelessly powering them.

Some of the specific accomplishments:

New fabrication approaches - we developed a simple fabrication technique, which in a single step transfers metal micro patterns to free standing silk films under ambient processing conditions. We refer to this process as "Silk Transfer Applied Micro Pattering" or STAMP for short. Additionally, this method adds versatility and utility to silk protein device fabrication by allowing the use of the patterned films as hard masks for oxygen based reactive ion etching (RIE). This method allows parallel fabrication of microstructures on large area, free standing and flexible silk films with high precision and eliminating the need for alignment. We have also demonstrated the use of this technique with various materials as masks for silk biopolymer RIE processing and a variety of SRR MM designs. This approach allows large area fabrication and is amenable to the transfer of different materials beyond metals. Individual feature sizes can be scaled to larger sizes to manufacture, for instance, metallic electrodes on silk films, or scaled down to the nanoscale for applications in photonic and plasmonic sensor systems

Transfer on arbitrary and curvilinear surfaces – Micro-/nano- metallic patterns were successfuly fabricated to serve as passive antenna sensors on an all protein-based silk substrates that were conformally transferred and adhered to curved surfaces. This process allows the intimate contact of micro- and nano-structures that can probe their surrounding environment with surfaces of evolving properties, allowing changes to be monitored. This approach was applied to in situ monitoring of food quality. It is to be noted that this type of sensor consists of all edible and biodegradable components - though it can also function as needed before consumption to monitor food quality, and then when the food is ready to be consumed, the portion of the food with the antenna on it can be readily sliced off and disposed of - holding utility and potential relevance for healthcare and food/consumer products and markets. Furthermore, the silk sensors presented in this work can serve as a platform to be integrated with other organic electronic and optoelectronic components which provide a promising path to a new set of biocompatible and eco-friendly conformal multi-functional devices.

Nanoimprinting on active silks/fluorescent silks - We have demonstrated directional and wavelength-specific fluorescent enhancement in rapidly manufactured, nanoimprinted silk films doped with various fluorophores. The enhancement is due to resonant coupling between the dopant emission and the lattice modes. The aqueous environment of silk fibroin solution used to generate the film makes it possible to easily mix a number of dyes (both organic and inorganic, including those used in biomedical applications). Moreover, the process of nanoimprinting silk is significantly faster (~1 min) and easier than conventional polymer patterning techniques. Patterned doped silk films are a new type of material with the potential to be incorporated as sensors, spectral filters, and light emitting devices for biological applications. Optically functionalized silk also holds promise for a new direction of research as biologically-based photonic crystal lasers or optical resonator structures.

Silk-based device transfer on arbitrary surfaces - We introduced a transfer method based on silk to put micro- and nanoscale devices on arbitrary surfaces. We transfered metamaterial (MM) devices on paper. This can be potentially utilized for quantitative analysis in biochemical sensing applications. Planar metallic resonators with minimum features of less than 5 μm have been fabricated on paper, using a photoresist-free shadow mask deposition technique. The fabricated paper metamaterial devices show unique electromagnetic (EM) resonant responses at predefined frequencies in dependence of the resonator size (i.e. TeraHertz frequencies in the current case - 1 THz = 10^{12} Hz). Proof of concept demonstrations have been accomplished by monitoring the resonance shift induced by placing different concentrations of glucose solution on the paper MM. These preliminary results of glucose sensing using paper-based MMs showed sensitivity of ~ 0.95 GHz/(mg/dl), and an associated ability to experimentally measure glucose level of 10 mg/dL, which can be further improved by optimizing the SRRs geometries and the characterization system. Extension of these systems to different frequency ranges is currently in progress.

Manufacturing micro- and nanoscale features on silk films and other silk material forms (fibers, gels, electrospun mats) – This processing progressed. Specifically of interest are the approaches to nanoimprinting. While use of the flip-chip bonder as a tool for nanoimprinting has been successful, it is still not practical for everyday use. As a result, a portable imprinting tool was developed to stamp standard 1-inch diameter silk films. The concept serves as a base for credit-card sized portable imprinting. A small footprint imprinter was developed and preliminary results were obtained. Besides reproducible imprinting on the nanoscale, the portable imprinter was used to study multilayered silks and silk-silk composites obtained by thermal bonding of different silk films.

Biomaterials chemistry, optics and functionalization – The direct inclusion of dopants (organic or inorganic) or the use of surface chemistries to add function to silk were successful directions pursued. Among the most interesting modifications of silk were the explorations of silk solution doped with Au-nanoparticles (NP). This silk can be transformed in multiple material formats (films, fibers, sponges, gels) maintaining a high concentration of Au-NP without aggregation, and allowing for thermal management of the film via optical excitation. Similar approaches were addressed with carbon nanotubes. Recent results included:

Gold Nanoparticle-Doped Silk Films for Wireless Power - We interfaced gold nanoparticle (GNP) doped silk films on thermoelectric chips for use to wireless power micro-devices. Proof-of-concept experiments were conducted by casting a GNP doped silk film on a miniature thermal-power chip, which generated ~20 mW when illuminated by a green laser with an output power of 450 mW/mm^2 at 532 nm. An interesting possibility, by altering the doping, is to power devices with a laser pointer.

Chemically modified silk for information storage – We worked on characterization of the chemically modified silk for information storage and demonstrated that azo-modified silk showed optical nonlinearities that were similar to those found in other azo-polymers including optically induced birefringence, holographic storage capability, and optically recorded surface relief gratings. Thermal effects due to laser related absorptive heating were monitored and shown to contribute minimally to the optical effects, especially at fluences of $100mWcm^{-2}$ and below. Future directions would include the applicability of optical control to biomedical sensing, tissue engineering and drug delivery.

Optical component design - The multifunctional silk platform with the modifications listed above and the potential interfaces listed above lends itself to the design of an unusual class of optical devices. A cadre of devices was demonstrated in the program and summarized in the patents and publications. The experimental efforts with different microprism silk reflectors were completed.

Additional modules:

The theme of the additional modules was the pursuit of the integration of chemical communication technologies with broader themes of silk biocompatibility and bio-resorbability. Devices were tested in-vivo as interfaces to living tissue and the human body. The animal studies in support were run through our NIH Center. The two themes for these studies were:

1. the potential for implantable and fully degradable electronic and optical devices for medical diagnosis and repair options, and

2. the stabilization capabilities of silk with labile compounds.

Some of the research included

- **silk reflectors/mirrors** - We used therapeutic drug-doped microprism reflectors for in-vivo experiments. The signal decreased as a function of microprism degradation to provide a measure of how much drug was eluted from the mirror. The implication is enabling for a future class of optical devices that become fully integrated into regenerated native tissues over time once their diagnostic utility is exhausted, eliminating the need for retrieval and extending the utility of *in-vivo* screening modalities. The results bear particular promise given the implications of individualized monitoring of drug delivery in vivo and the concepts for multifunctional devices enabled by this approach, where a single device can administer a therapeutic compound while providing information of disease progression. The utility of multifunctional bioresorbable devices goes beyond medical applications into environmental monitoring or food chain safety, where such devices could be used without negative impact on the environment or the consumer.

- Extended studies of implanted silk electronic devices to assess biological responses. Prototypes were developed for silk/electronic implantable programmable heaters powered by wireless coils for inductive power transfer.

- Experiments focused on immobilization and entrapment of biological agents in silk, including enzymes, antibodies, small molecules and therapeutics to assess stability and biological function when entrapped in silk. Also the mechanisms involved were determined in part, and temperature stabilization options were also studied as part of the effort. Notably, antibiotics like penicillin can be stabilized at higher temperatures, as can a range of other labile compounds such as vaccines, to demonstrate both the breadth and utility of the technology.

- As part of the efforts above, we developed silk microneedle systems, using micromolding techniques. These devices provide direct delivery options for the above compounds combined with the stabilization impact as described above. These devices have broad implications for soldiers to consumers, for example, as pocket-carried medicines that can be carried at room temperature and higher for months without loss of function, while usable for application as a band aide when needed. Thus, fieldable therapeutics, wound treatments and nutrients to control alertness levels are just some of the envisioned opportunities for this broad based technology.

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Peer-reviewed publications

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2. Omenetto FG, Kaplan DL. A new route for silk. *Nature Photonics*, 2(11): 641-643, (2008).
3. Perry H, Gopinath A, Kaplan DL, Negro LD, Omenetto FG. Nano- and micropatterning of optically transparent, mechanically robust, biocompatible silk fibroin films. *Adv Materials*, 20(16): 3070-3072 (2008).

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4. Adato R, Yanik AA, Amsden JJ, Kaplan DL, Omenetto FG, Hong MK, Srramilli S, Altug H. Ultra-sensitive vibrational spectroscopy of protein monolayers with plasmonic nanoantenna arrays. *Proc Natl Acad Sci USA*, 106(46): 19227-19232, (2009). [PMCID: PMC2770897]
5. Amsden JJ, Perry H, Boriskina SV, Gopinahth A, Kaplan DL, Dal Negro L, Omenetto FG. Spectral analysis of induced color change on periodically nanopatterned silk films. *Opt Express*, 17(23): 21271-21279, (2009). [PMID: 19997366]
6. Kim DH, Kim YS, Amsden J, Panilaitis B, Kaplan DL, Omenetto FG, Zakin MR, JA Rogers. Silicon electronics on silk as a path to resorbable implantable devices. *Appl Phys Lett*, 95(13): 133701, (2009). [PMCID: PMC2816979]
7. Lawrence B, Omenetto FG, Kaplan DL. Processing methods to control silk fibroin film biomaterial features. *J Mater Sci,* 43(21): 6967-6985, (2009).
8. Lu S, Wang X, Lu Q, Hu X, Uppal N, Omenetto FG, Kaplan DL. Stabilization of enzymes in silk films. *Biomacromolecules*, 10(5): 1032-1042, (2009). [PMCID: PMC2705530]

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9. Amsden JJ, Domachuk P, Gopinath A, White RD, Negro LD, Kaplan DL, Omenetto FG. Rapid nanoimprinting of silk fibroin films for biophotonic applications. *Adv Mater,* 22(15): 1746-1749, (2010). [PMID: 20496408]
10. Domachuk P, Tsioris K, Omenetto FG, Kaplan DL. Bio-microfluidics: biomaterials and biomimetic designs. *Adv Materials,* 22(2): 249-260, (2010). [PMID: 20217686]
11. Kim DH, Viventi J, Amsden JJ, Vigeland L, Kim YS, Blanco JA, Panilaitis B, Frechette ES, Contreras D, Kaplan DL, Omenetto FG, Huang Y, Hwang KC, Zakin MR, Litt B, Rogers JA. Dissolvable films of silk fibroin for ultrathin conformal biointegrated electronics. *Nat Mater*, 9(6): 511-517, (2010). [PMCID: PMC3034223]
12. Kim RH, Kim DH, Xiao J, Kim BH, Park SI, Panilaitis B, Ghaffari R, Yao J, Li M, Liu Z, Malyarchuk V, Kim DG, Lee AP, Nuzzo RG, Kaplan DL, Omenetto FG, Huang Y, Kang Z, Rogers JA. Waterproof AlInGaP optoelectronics on stretchable substrates with applications in biomedicine and robotics. *Nat Mater*, 9(11): 929-937, (2010). [PMID: 209531185]
13. Lawrence B, D., S. Wharram, J. A. Kluge, G. G. Leisk, F. G. Omenetto, M. I. Rosenblatt, Kaplan DL. Effect of hydration on silk film materials properties. *Macromol Biosci*, 10(4): 393-403, (2010). [PMCID: PMC3142628]

14. Lee SY, Amsden JJ, Boriskina SV, Gopinath A, Mitropolous A, Kaplan DL, Omenetto FG, Negro LD. Spatial and spectral detection of protein monolayers with deterministic aperiodic arrays of metal nanoparticles. *Proc Natl Acad Sci USA*, 107(27): 12086-12090, (2010). [PMCID: PMC2901425]
15. Lu Q, Wang X, Hu X, Cebe P, Omenetto F, Kaplan DL. Stabilization and release of enzymes from silk films. *Macromol Biosci*, 10(4): 359-368, (2010). [PMID: 20217856]
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17. Mondia JP, Amsden JJ, Lin D, Negro LD, Kaplan DL, Omenetto FG. Rapid nanoimprinting of doped silk films for Enhanced fluorescent emission. *Adv Mater*, 22(41): 4596-4599, (2010). [PMID: 20859936]
18. Omenetto FG, Kaplan DL. SnapShot: silk biomaterials. *Biomaterials*, 31(23): 6119-6120, (2010). [PMID: 20593549]
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20. Tao H, Amsden JJ, Strikwerda AC, Fan K, Kaplan DL, Zhang X, Averitt RD, Omenetto FG. Metamaterial silk composites at terahertz frequencies. *Adv Mater*, 22(32): 3527-3531, (2010). [PMID: 20665563]

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21. Tao H, Chieffo LR, Brenckle MA, Siebert SM, Liu M, Strikwerda AC, Fan K, Kaplan DL, Zhang X, Averitt RD, Omenetto FG. Metamaterials on paper as a sensing platform. *Adv Mater*, 23(28): 3197-3201, (2011). [PMID: 21638342]
22. Tsioris K, Tao H, Liu M, Hopwood JA, Kaplan DL, Averitt RD, Omenetto FG. Rapid transfer-based micropatterning and dry etching of silk microstructures. *Adv Mater*, 23(17): 2015-2019, (2011). [PMCID: PMC3401411]

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25. Tao H, Brenckle MA, Yang M, Zhang J, Liu M, Siebert SM, Averitt RD, Mannoor MS, McAlpine MC, Rogers JA, Kaplan DL, Omenetto FG. Silk-based conformal, adhesive, edible food sensors. *Adv Mater*, 24(8): 1067-1072, (2012). [PMID: 22266768]
26. Tao H, Kaplan DL, Omenetto FG. Silk materials - a road to sustainable high technology. *Adv Mater*, 24(21): 2824-2837, (2012). [PMID: 22553118]

Presentations at meetings, but not published in Conference Proceedings ______________________ 7

Silk photonics, UC Irvine (2011)
Silk – the ancient material of the future, TED, Long Beach, CA (2011)
Flex Electronics, Lemelson Prize Colloquium, MIT (2011)
Silk Photonics, New York Academy of Sciences (2011)
Silk Technology – Plenary talk at Singapore ICYRAM-MRS (2012)
Inspiring Matter – Royal College of Art London (2012)
Silk Workshop, France, DoD sponsored (2012)