REPORT DOCUMENTATION PAGE

Form Approved OMB NO. 0704-0188

1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE	3. DATES COVERED (From - To)
01-09-2016	Final Report	1-Jun-2012 - 31-Dec-2015

4. TITLE AND SUBTITLE
Final Report: Nanoscale Magnetic Resonance Imaging and Characterization of Organic Electronic Materials

5a. CONTRACT NUMBER
W911NF-12-1-0221

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
611102

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

6. AUTHORS
John A. Marohn

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES
Cornell University
Office of Sponsored Programs
373 Pine Tree Road
Ithaca, NY 14850 -2820

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES)
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSOR/MONITOR'S ACRONYM(S)
ARO

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
60703-MS.6

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

13. SUPPLEMENTARY NOTES
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
This report describes work accomplished under the U.S. Army Research Office grant “Nanoscale magnetic resonance imaging and characterization of organic electronic materials” (P.I.: John A. Marohn, Cornell University; grant no. W911NF-12-1-0221; 06/01/2012 to 05/30/2016). The main accomplishment of the grant was the development of a magnetic resonance force microscope capable of detecting magnetic resonance signal from an organic semiconductor device as thin as ca 50 nm. The microscope employs a magnet-tipped attonewton-sensitivity

15. SUBJECT TERMS
materials science, magnetic resonance, nuclear magnetic resonance, dynamic nuclear polarization, magnetic resonance force microscopy, scanned probe microscopy, organic semiconductor, nanocharacterization

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			John Marohn
UU	UU	UU	UU		19b. TELEPHONE NUMBER 607-255-2004

Report Title

Final Report: Nanoscale Magnetic Resonance Imaging and Characterization of Organic Electronic Materials

ABSTRACT

This report describes work accomplished under the U.S. Army Research Office grant “Nanoscale magnetic resonance imaging and characterization of organic electronic materials” (P.I.: John A. Marohn, Cornell University; grant no. W911NF-12-1-0221; 06/01/2012 to 05/30/2016). The main accomplishment of the grant was the development of a magnetic resonance force microscope capable of detecting magnetic resonance signal from an organic semiconductor device as thin as ca 50 nm. The microscope employs a magnet-tipped attonewton-sensitivity microcantilever, operates with the sample in vacuum at a temperature of 4.2 kelvin, and is capable of mechanically detecting, in a single experiment, electron spin resonance at fields up to 0.6 tesla and nuclear magnetic resonance at fields up to 9 tesla. The unique capabilities of this microscope enabled the observation of hyperpolarized proton magnetization in a nitroxide-doped polymer film using dynamic nuclear polarization in concert with mechanically detected magnetic resonance. In this report we describe what we have learned during the course of the grant and how we can apply these new insights to achieve (1) the proposed magnetic resonance characterization and imaging of organic semiconductor devices and (2) the long-term goal of imaging individual macromolecular complexes by magnetic resonance force microscopy.

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
08/31/2016	1	Corinne E. Issac, Christine M. Gleave, Paméla T. Nasr, Hoang L. Nguyen, Elizabeth A. Curley, Jonilyn L. Yoder, Eric W. Moore, Lei Chen, John A. Marohn. Dynamic nuclear polarization in a magnetic resonance force microscope experiment, Phys. Chem. Chem. Phys., ( ): 8806. doi:
TOTAL:		**1**

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

1. J. A. Marohn, Charting a path to 1 nm resolution magnetic resonance imaging of biomacromolecules: High-gradient magnet-tipped cantilevers and dynamic nuclear polarization in magnetic resonance force microscopy, NanoMRI Conference 2012; Ascona, Switzerland; July 22 – 27, 2012, URL http://www.spin.ethz.ch/NanoMRI. Invited talk at international conference.

2. J. G. Longenecker, H. J. Mamin, A. W. Senko, L. Chen, C. T. Rettner, D. Rugar, and J. A. Marohn, High gradient cobalt nanomagnets integrated on attonewton-sensitivity cantilevers for scanned probe magnetic resonance detection of nuclear spins, Gordon Research Conference on Nanostructure Fabrication; Biddeford, Maine; July 15 – 20, 2012, URL http://www.grc.org/programs.aspx?year=2012&program=nanofab. Contributed talk at national conference.

3. J. G. Longenecker, H. J. Mamin, A. W. Senko, L. Chen, C. T. Rettner, D. Rugar, and J. A. Marohn, Development and characterization of high-gradient cobalt-tipped cantilevers, NanoMRI Conference 2012; Ascona, Switzerland; July 22 – 27, 2012, URL http://www.spin.ethz.ch/NanoMRI. Contributed talk at international conference.

4. J. G. Longenecker, H. J. Mamin, A. W. Senko, L. Chen, C. T. Rettner, D. Rugar, and J. A. Marohn, High gradient nanomagnets on cantilevers used for NMR-MRFM force detection, NanoMRI Conference 2012; Ascona, Switzerland; July 22 – 27, 2012, URL http://www.spin.ethz.ch/NanoMRI. Contributed poster at international conference.

5. L. Chen, J. G. Longenecker, E. W. Moore, and J. A. Marohn, MRFM detection of a large slowly relaxing spin polarization induced by ESR, NanoMRI Conference 2012; Ascona, Switzerland; July 22 – 27, 2012, URL http://www.spin.ethz.ch/NanoMRI. Contributed poster at international conference.

6. L. Chen, J. G. Longenecker, E. W. Moore, and J. A. Marohn, Magnetic Resonance Force Microscopy Detected Long-Lived Spin Magnetization Signal by Electron Spin Saturation, 12th MMM-Intermag Conference; Chicago, Illinois; Jan 14 – 18, 2013. Contributed talk at national conference.

7. J. A. Marohn, Nanoscale Functional Imaging of Organic Materials: Using cantilevers to detect magnetic resonance, spectroscopically probe electronic energy levels, image charge generation, and study charge diffusion at the nanoscale, University of California, Santa Barbara; April 29, 2013. Invited university talk.

8. J. A. Marohn, Nanoscale Functional Imaging of Organic Materials, University of California, Riverside; May 21, 2013. Invited university talk.

9. J. A. Marohn, Nanoscale Functional Imaging of Organic Materials, University of Leiden, the Netherlands; September 18, 2013. Invited talk at international university.

10. J. A. Marohn, Probing Light-Driven and Thermally-Driven Charge Dynamics in Organic Semiconductor Films with Frequency-Modulated Scanning Kelvin Probe Microscopy, International Conference on Scanning Probe Microscopy on Soft and Polymeric Materials 2014; Toronto, Canada; September 2 – 6, 2014, URL http://www.spm-p.org/spm-on-spm-2014.aspx. Invited talk at international conference.

11. J. A. Marohn, Nanoscale Functional Imaging of Organic Materials, Student-hosted colloquium; Stanford University, Palo Alto, California; October 27, 2014. Invited university talk.

12. H. L. Nguyen and J. A. Marohn, Investigating Image Reconstruction Methods for Magnetic Resonance Force Microscopy, 2015 Northeast Regional Meeting of the American Chemical Society; Ithaca, New York; June 10 – 13, 2015. Contributed talk at regional conference.

13. C. E. Isaac, C. Gleave, P. Nasr, and J. A. Marohn, Enhancing Nuclear Polarization for Nanoscale Magnetic Resonance Imaging, 2015 Northeast Regional Meeting of the American Chemical Society; Ithaca, New York; June 10 – 13, 2015. Contributed talk at regional conference.

14. H. L. Nguyen and J. A. Marohn, Image reconstruction in nanoscale magnetic resonance imaging, 5th International nano-MRI conference; Institute for Quantum Computing; University of Waterloo, Canada; July 26 – 31, 2015. Contributed poster at international conference.

15. C. Isaac, C. Gleave, P. Nasr, H. L. Nguyen, and J. A. Marohn, Enhancing nuclear polarization for nanoscale magnetic resonance imaging, 5th International nano-MRI conference; Institute for Quantum Computing; University of Waterloo, Canada; July 26 – 31, 2015. Contributed poster at international conference.

16. J. A. Marohn, A Microscope for Imaging Individual Macromolecules, 5th International Nano-MRI Conference; Institute for Quantum Computing; University of Waterloo, Canada; July 26 – 31, 2015, URL https://uwaterloo.ca/nanomri/. Invited talk at international conference.

17. J. A. Marohn, N/A; invitation declined, International Society of Magnetic Resonance Meeting; East China Normal University, Shanghai, China; August 16 – 21, 2015, URL http://ismar2015.ecnu.edu.cn. Declined because it conflicted with my duties as Director of Undergraduate Studies for the Department of Chemistry and Chemical Biology at Cornell. Invited talk at international conference.

18. J. A. Marohn, Nanoscale Functional Imaging of Organic Materials, Dept. of Mechanical Engineering Colloquium; State University of New York at Binghamton, Binghamton, New York; November 19, 2015. Invited university talk.

Number of Presentations: 18.00

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

TOTAL:

Number of Manuscripts:

Books

Received Book

TOTAL:

Received Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

Corinne E. Isaac; Summer Fellowship, American Chemical Society, Analytical Division; 2016.

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
Ms. Jonilyn Yoder (née Longencke	1.00	
Ms. Christine Gleave	1.00	
Ms. Paméla Nasr	1.00	
Ms. Corinne Isaac (née Kingley)	0.05	
Mr. Hoang Nguyen	0.05	
Ms. Elizabeth Curley	0.05	
Ms. Sarah Nathan	0.05	
Mr. Michael Boucher	0.00	
FTE Equivalent:	**3.20**	
Total Number:	**8**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
John A. Marohn	0.08	
FTE Equivalent:	**0.08**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED	Discipline
Mr. Alexander Senko	0.25	Materials Science and Engineering
Ms. Xueying (Sherry) Li	0.25	Chemistry
FTE Equivalent:	**0.50**	
Total Number:	**2**	

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:...... 1.00

Names of Personnel receiving masters degrees

NAME	
Ms. Christine Gleave	
Total Number:	**1**

Names of personnel receiving PHDs

NAME	
Ms. Jonilyn Yoder (née Longencker)	
Total Number:	**1**

Names of other research staff

NAME	PERCENT_SUPPORTED
Mr. Alexander Senko	1.00
FTE Equivalent:	**1.00**
Total Number:	**1**

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See Attachment

Technology Transfer

In the Fall of 2013, Marohn was contacted by Dr. Andrew Harter who leads a team developing a magnetic resonance force microscope at the Oak Ridge National Laboratory. On February 6, 2014, Dr. Harter and his collaborators flew to Ithaca, New York, for a long day of technical discussions with Marohn and his team at Cornell. The visitors included Andrew Harter (Oak Ridge National Laboratory; DOE), Heath Huckabay (Oak Ridge National Laboratory; DOE), Matthew Wellons (Savannah River National Laboratory; DOE), and Christopher Klug (U.S. Naval Research Laboratory). The goal of the visit was to use the Marohn team's experience in designing and constructing a magnetic resonance force microscope to help the Oak Ridge team make key design decisions for a microscope they are building. During the visit, the two teams identified areas of possible collaboration, such as developing sample-locating protocols. The trip moreover spurred Marohn and co-workers to release their cantilever-analysis and signal-simulation software into the public domain.

Marohn and his team released their algorithms for extracting the time-dependent frequency of an oscillator into the public domain as a Python package, FreqDemod, on 01/24/2015 under the GNU General Public License, Version 3. The release consists of three components: (1) python package, https://pypi.python.org/pypi/FreqDemod, available on the Python Package Index for installation on any computer running Python using the pip install mechanism; (2) source code, https://github.com/JohnMarohn/FreqDemod, freely available on GitHub for anyone to download or modify. Interested parties can submit code revisions to the main code repository using GitHub's pull request feature; and (3) documentation, http://FreqDemod.rtd.org, released through the free ReadTheDocs service. The documentation includes an ipython notebook showing how to use the package's code to extract the time-dependent frequency and amplitude of a sine-wave oscillation. The release includes over 1900 lines of code, including extensive in-line documentation; a first-principles derivation of cantilever thermomechanical fluctuations and force noise; and an exhaustive first-principles derivation of cantilever phase and frequency noise.

In February 2016, we modified the FreqDemod package to be Python 3.4 compatible. This modification was in response to a request by Ray Schumacher, a Programmer/Engineer at Jan Medical, Inc. (http://janmedical.com; 110 Pioneer Way, Suite L; Mountain View, CA 94041). The company produces a headset with embedded sound pressure-level sensors for diagnosing concussions.

Continuing a long-standing collaboration, Professor Lee Harrell of the U.S. Military Academy visited the Cornell magnetic resonance force micrsocope laboratory on December 16 – 18, 2013; July 28 – August 1, 2014; December 14 – 18, 2015; and January 11 – 15, 2016. Professor Harrell is working with cadets at the U.S. Military Academy to numerically simulate the effect of electrical oscillator phase noise in the parametric-upconversion magnetic resonance force microscope experiment invented at Cornell (E. W. Moore, S.-G. Lee, S. A. Hickman, L. E. Harrell, and J. A. Marohn, Evading surface and detector frequency noise in harmonic oscillator measurements of force gradients, Appl. Phys. Lett., 2010, 97, 044105, URL http://dx.doi.org/10.1063/1.3465906). He has served as a beta-tester for our open-source frequency-demodulation code, FreqDemod, discussed above.

ARO Grant W911NF-12-1-0221
Final Report
John A. Marohn (P.I.)
Cornell University

September 1, 2016

KEYWORDS: materials science, magnetic resonance, nuclear magnetic resonance, dynamic nuclear polarization, magnetic resonance force microscopy, scanned probe microscopy, organic semiconductor, nanocharacterization

Abstract

This report describes work accomplished under the U.S. Army Research Office grant "Nanoscale magnetic resonance imaging and characterization of organic electronic materials" (P.I.: John A. Marohn, Cornell University; grant no. W911NF-12-1-0221; 06/01/2012 to 05/30/2016). The main accomplishment of the grant was the development of a magnetic resonance force microscope capable of detecting magnetic resonance signal from an organic semiconductor device as thin as *ca* 50 nm. The microscope employs a magnet-tipped attonewton-sensitivity microcantilever, operates with the sample in vacuum at a temperature of 4.2 kelvin, and is capable of mechanically detecting, in a single experiment, electron spin resonance at fields up to 0.6 tesla and nuclear magnetic resonance at fields up to 9 tesla. The unique capabilities of this microscope enabled the observation of hyperpolarized proton magnetization in a nitroxide-doped polymer film using dynamic nuclear polarization in concert with mechanically detected magnetic resonance. In this report we describe what we have learned during the course of the grant and how we can apply these new insights to achieve (1) the proposed magnetic resonance characterization and imaging of organic semiconductor devices and (2) the long-term goal of imaging individual macromolecular complexes by magnetic resonance force microscopy.

Submissions or publications

(a) Papers published in peer-reviewed journals: 1

C. E. Isaac, C. M. Gleave, P. T. Nasr, H. L. Nguyen, E. A. Curley, J. L. Yoder, E. W. Moore, L. Chen, and J. A. Marohn, Dynamic nuclear polarization in a magnetic resonance force microscope experiment, *Phys. Chem. Chem. Phys.*, **2016**, *18*, 8806 – 8819, URL http://dx.doi.org/10.1039/C6CP00084C. The manuscript is 14 pages long and consists of 9 figures, 2 tables, and 58 references. The supporting-information document is 6 page long and consists of 4 figures, 1 table, and 11 references.

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

None to report.

(c) Presentations

i. Presentations at meetings, but not published in Conference Proceedings: 18

1. J. A. Marohn, *Charting a path to 1 nm resolution magnetic resonance imaging of biomacromolecules: High-gradient magnet-tipped cantilevers and dynamic nuclear polarization in magnetic resonance force microscopy*, NanoMRI Conference 2012; Ascona, Switzerland; July 22 – 27, **2012**, URL http://www.spin.ethz.ch/NanoMRI. Invited talk at international conference.
2. J. G. Longenecker, H. J. Mamin, A. W. Senko, L. Chen, C. T. Rettner, D. Rugar, and J. A. Marohn, *High gradient cobalt nanomagnets integrated on attonewton-sensitivity cantilevers for scanned probe magnetic resonance detection of nuclear spins*, Gordon Research Conference on Nanostructure Fabrication; Biddeford, Maine; July 15 – 20, **2012**, URL http://www.grc.org/programs.aspx?year=2012&program=nanofab. Contributed talk at national conference.
3. J. G. Longenecker, H. J. Mamin, A. W. Senko, L. Chen, C. T. Rettner, D. Rugar, and J. A. Marohn, *Development and characterization of high-gradient cobalt-tipped cantilevers*, NanoMRI Conference 2012; Ascona, Switzerland; July 22 – 27, **2012**, URL http://www.spin.ethz.ch/NanoMRI. Contributed talk at international conference.
4. J. G. Longenecker, H. J. Mamin, A. W. Senko, L. Chen, C. T. Rettner, D. Rugar, and J. A. Marohn, *High gradient nanomagnets on cantilevers used for NMR-MRFM force detection*, NanoMRI Conference 2012; Ascona, Switzerland; July 22 – 27, **2012**, URL http://www.spin.ethz.ch/NanoMRI. Contributed poster at international conference.
5. L. Chen, J. G. Longenecker, E. W. Moore, and J. A. Marohn, *MRFM detection of a large slowly relaxing spin polarization induced by ESR*, NanoMRI Conference 2012; Ascona, Switzerland; July 22 – 27, **2012**, URL http://www.spin.ethz.ch/NanoMRI. Contributed poster at international conference.
6. L. Chen, J. G. Longenecker, E. W. Moore, and J. A. Marohn, *Magnetic Resonance Force Microscopy Detected Long-Lived Spin Magnetization Signal by Electron Spin Saturation*, 12th MMM-Intermag Conference; Chicago, Illinois; Jan 14 – 18, **2013**. Contributed talk at national conference.
7. J. A. Marohn, *Nanoscale Functional Imaging of Organic Materials: Using cantilevers to detect magnetic resonance, spectroscopically probe electronic energy levels, image charge generation, and study charge diffusion at the nanoscale*, University of California, Santa Barbara; April 29, **2013**. Invited university talk.

8. J. A. Marohn, *Nanoscale Functional Imaging of Organic Materials*, University of California, Riverside; May 21, **2013**. Invited university talk.
9. J. A. Marohn, *Nanoscale Functional Imaging of Organic Materials*, University of Leiden, the Netherlands; September 18, **2013**. Invited talk at international university.
10. J. A. Marohn, *Probing Light-Driven and Thermally-Driven Charge Dynamics in Organic Semiconductor Films with Frequency-Modulated Scanning Kelvin Probe Microscopy*, International Conference on Scanning Probe Microscopy on Soft and Polymeric Materials 2014; Toronto, Canada; September 2 – 6, **2014**, URL http://www.spm-p.org/spm-on-spm-2014.aspx. Invited talk at international conference.
11. J. A. Marohn, *Nanoscale Functional Imaging of Organic Materials*, Student-hosted colloquium; Stanford University, Palo Alto, California; October 27, **2014**. Invited university talk.
12. H. L. Nguyen and J. A. Marohn, *Investigating Image Reconstruction Methods for Magnetic Resonance Force Microscopy*, 2015 Northeast Regional Meeting of the American Chemical Society; Ithaca, New York; June 10 – 13, **2015**. Contributed talk at regional conference.
13. C. E. Isaac, C. Gleave, P. Nasr, and J. A. Marohn, *Enhancing Nuclear Polarization for Nanoscale Magnetic Resonance Imaging*, 2015 Northeast Regional Meeting of the American Chemical Society; Ithaca, New York; June 10 – 13, **2015**. Contributed talk at regional conference.
14. H. L. Nguyen and J. A. Marohn, *Image reconstruction in nanoscale magnetic resonance imaging*, 5th International nano-MRI conference; Institute for Quantum Computing; University of Waterloo, Canada; July 26 – 31, **2015**. Contributed poster at international conference.
15. C. Isaac, C. Gleave, P. Nasr, H. L. Nguyen, and J. A. Marohn, *Enhancing nuclear polarization for nanoscale magnetic resonance imaging*, 5th International nano-MRI conference; Institute for Quantum Computing; University of Waterloo, Canada; July 26 – 31, **2015**. Contributed poster at international conference.
16. J. A. Marohn, *A Microscope for Imaging Individual Macromolecules*, 5th International Nano-MRI Conference; Institute for Quantum Computing; University of Waterloo, Canada; July 26 – 31, **2015**, URL https://uwaterloo.ca/nanomri/. Invited talk at international conference.
17. J. A. Marohn, *N/A; invitation declined*, International Society of Magnetic Resonance Meeting; East China Normal University, Shanghai, China; August 16 – 21, **2015**, URL http://ismar2015.ecnu.edu.cn. Declined because it conflicted with my duties as Director of Undergraduate Studies for the Department of Chemistry and Chemical Biology at Cornell. Invited talk at international conference.
18. J. A. Marohn, *Nanoscale Functional Imaging of Organic Materials*, Dept. of Mechanical Engineering Colloquium; State University of New York at

Binghamton, Binghamton, New York; November 19, **2015**. Invited university talk.

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

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

(d) Manuscripts: 0

None to report.

(e) Books: 1

J. G. Longenecker *High-Gradient Nanomagnet-on-Cantilever Fabrication for Scanned Probe Detection of Magnetic Resonance* PhD thesis, Cornell University, Ithaca, New York, **2013**, URL http://hdl.handle.net/1813/33775. Note: 130 MB.

(f) Honor and Awards: 1

Corinne E. Isaac; Summer Fellowship, American Chemical Society, Analytical Division; 2016.

(g) Title of Patents Disclosed during the reporting period: 0

None to report.

(h) Patents Awarded during the reporting period: 0

None to report.

Student/Supported Personnel Metrics for this Reporting

(a) Graduate Students: 8

Ms. Jonilyn Yoder (née Longencker). 1.0 FTE in summer 2012 and AY 2012 – 2013. Salary and supplies. Graduated with Ph.D. in Chemistry in 2013.

Ms. Christine Gleave. 1.0 FTE in summer 2013 and AY 2013 – 2014. Salary and supplies. Graduated with M.S. in Chemistry in 2014.

Ms. Paméla Nasr. 1.0 FTE in AY 2013 – 2014, summer 2014, and AY 2014 – 2015. Salary and supplies.

Ms. Corinne Isaac (née Kingley). Supplemental summer support in 2014. Supplies AY 2013 – 2014, summer 2014, AY 2014 – 2015, and AY 2015 – 2016.

Mr. Hoang Nguyen. Supplemental summer support in 2014. Supplies AY 2013 – 2014, summer 2014, and AY 2014 – 2015.

Ms. Elizabeth Curley. Supplemental summer support in 2014. Supplies summer 2014, AY 2014 – 2015, and AY 2015 – 2016.

Ms. Sarah Nathan. Supplemental summer support in 2013.

Mr. Michael Boucher. Supplies AY 2015 – 2016.

(b) Post Doctorates: 0

(c) Faculty: 1.

Dr. John A. Marohn. 0.5 month summer salary in summer 2013.

(d) Undergraduate Students: 2

Mr. Alexander Senko. 1.0 FTE in summer 2012; part time AY 2012 – 2013; and 1.0 FTE in summer 2013. Graduated in 2013 with a B.S. in Materials Science and Engineering.

Ms. Xueying (Sherry) Li. 1.0 FTE in summer 2015. Graduated in 2015 with a B.A. in Chemistry.

(e) Graduating Undergraduate Metrics: 2

Mr. Alexander Senko was funded as an undergraduate researcher and, following graduation, as research staff by this grant in Years 1 and 2. In the fall of 2013, Alex joined the Materials Science and Engineering Ph.D. program at MIT, where he carries out research in the Bioelectronics Group of Professor Polina Anikeeva (URL http://www.rle.mit.edu/bioelectronics/). In the spring of 2014, Alex was awarded a National Defense Science and Engineering Graduate Fellowship.

Ms. Xueying (Sherry) Li was funded as a summer undergraduate researcher by this grant in Year 3. In the Fall of 2016 Ms. Li will enter the Ph.D. program of the Materials Science and Engineering Department at the University of California, San Diego.

i. Number who graduated during this period: 2
ii. Number who graduated during this period with a degree in science, mathematics, engineering, or technology fields: 2
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
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: 0
vi. Number who intend to work for the Department of Defense: 0
vii. Number who will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: 1

(f) Masters Degrees Awarded: 1

C. Gleave, Micron-scale coplanar waveguides to enable nanoscale magnetic resonance imaging (nano-MRI). Master's thesis, Cornell University, Ithaca, New York; May 5, **2014**.

(g) Ph.D.s Awarded: 1

J. G. Longenecker *High-Gradient Nanomagnet-on-Cantilever Fabrication for Scanned Probe Detection of Magnetic Resonance* PhD thesis, Cornell University, Ithaca, New York, **2013**, URL http://hdl.handle.net/1813/33775.

Dr. Jonilyn Yoder (née Longenecker) was funded as a graduate student and postdoctoral fellow by this grant in Year 1. Since July 2013 she has been employed as a member of the technical staff at the MIT Lincoln Laboratories, working on the laboratory's superconducting qubits team. Her current work is of great interest to the Department of Defense; her team is funded by the Office of the Director of National Intelligence (ODNI), the Intelligence Advanced Research Projects Activity (IARPA), and Air Force Office of Scientific Research (AFOSR) (URL http://meetings.aps.org/Meeting/MAR14/Session/M36.4).

(h) Other Research staff: 1

Mr. Alexander Senko was employed full time in the summer of 2013 following his graduation from Cornell University.

Technology Transfer

In the Fall of 2013, Marohn was contacted by Dr. Andrew Harter who leads a team developing a magnetic resonance force microscope at the Oak Ridge National Laboratory. On February 6, 2014, Dr. Harter and his collaborators flew to Ithaca, New York, for a long day of technical discussions with Marohn and his team at Cornell. The visitors included Andrew Harter (Oak Ridge National Laboratory; DOE), Heath Huckabay (Oak Ridge National Laboratory; DOE), Matthew Wellons (Savannah River National Laboratory; DOE), and Christopher Klug (U.S. Naval Research Laboratory). The goal of the visit was to use the Marohn team's experience in designing and constructing a magnetic resonance force microscope to help the Oak Ridge team make key design decisions for a microscope they are building. During the visit, the two teams identified areas of possible collaboration, such as developing sample-locating protocols. The trip moreover spurred Marohn and coworkers to release their cantilever-analysis and signal-simulation software into the public domain.

Marohn and his team released their algorithms for extracting the time-dependent frequency of an oscillator into the public domain as a Python package, *FreqDemod*, on 01/24/2015 under the GNU General Public License, Version 3. The release consists of three components: (1) python package, https://pypi.python.org/pypi/FreqDemod, available on the Python Package Index for installation on any computer running Python using the *pip install* mechanism; (2) source code, https://github.com/JohnMarohn/FreqDemod, freely available on GitHub for anyone to download or modify. Interested parties can submit code revisions to the main code repository using GitHub's *pull request* feature; and (3) documentation, http://FreqDemod.rtd.org, released through the free ReadTheDocs service. The documentation includes an ipython notebook showing how to use the package's code to extract the time-dependent frequency and amplitude of a sine-wave oscillation. The release includes over 1900 lines of code, including extensive in-line documentation; a first-principles derivation of cantilever thermomechanical fluctuations and force noise; and an exhaustive first-principles derivation of cantilever phase and frequency noise.

In February 2016, we modified the FreqDemod package to be Python 3.4 compatible. This modification was in response to a request by Ray Schumacher, a Programmer/Engineer at Jan Medical, Inc. (http://janmedical.com; 110 Pioneer Way, Suite L; Mountain View, CA 94041). The company produces a headset with embedded sound pressure-level sensors for diagnosing concussions.

Continuing a long-standing collaboration, Professor Lee Harrell of the U.S. Military Academy visited the Cornell magnetic resonance force micrsocope laboratory on December 16 – 18, 2013; July 28 – August 1, 2014; December 14 – 18, 2015; and January 11 – 15, 2016. Professor Harrell is working with cadets at the U.S. Military Academy to numerically simulate the effect of electrical oscillator phase noise in the parametric-upconversion magnetic resonance force microscope experiment invented at Cornell (E. W. Moore, S.-G. Lee, S. A. Hickman, L. E. Harrell, and J. A. Marohn, Evading surface and detector frequency noise in harmonic oscillator measurements of force gradients, *Appl. Phys. Lett.*, **2010**, *97*, 044105, URL http://dx.doi.org/10.1063/1.3465906). He has served as a beta-tester for our open-source frequency-demodulation code, *FreqDemod*, discussed above.

Scientific Progress and Accomplishments

The starting point for this grant's work is the magnet-tipped attonewton-sensitivity cantilevers developed by the Cornell magnetic resonance force microscope (MRFM) team [Hickman 2010, Longenecker 2011]. In collaboration with Dan Rugar and John Mamin at IBM Almaden, these cantilevers were used to detect nuclear magnetic resonance from proton spins in a thin polystyrene film in vacuum at 4.2 kelvin, at a sensitivity of approximately 500 proton magnetic moments [Longenecker 2012]. This result suggested the possibility of using the Cornell cantilevers to detect and image nuclear magnetic resonance with a few-nanometer resolution in essentially any thin-film sample. The goal of this proposal was to develop a microwire thin-film sample platform for the Cornell magnetic resonance force microscope (MRFM) and, in combination with the Cornell cantilevers, use this sample platform to characterize organic semiconductor thin-film devices.

SPIN DETECTION

By the end of Year 1, we had completed the construction and testing of the major subsystems of our team's cryogenic magnetic resonance force microscope. We had furthermore demonstrated the ability to bring a high-compliance cantilever into near-contact with a surface in vacuum at a temperature of 4.2 kelvin. Years 2 and 3 were occupied with simulating micrometer-scale coplanar waveguides operating at frequencies up to 20 GHz; fabricating, electrically characterizing, and installing the waveguides into the Cornell microscope; and developing protocols for positioning a high-compliance cantilever over the waveguide at liquid helium temperatures. This work is described in detail in our previous reports.

In the last quarter of Year 3 we observed ^{1}H nuclear magnetic resonance at 6.0 tesla in our apparatus. This experiment employed an attonewton-sensitivity cantilever with a 7 micrometer-diameter nickel sphere tip. The sample was a 250 nm thick polystyrene film doped with the free-radical TEMPAMINE at a concentration of 40 mM. This experiment observed Curie-law magnetization from protons at temperature of 4.2 kelvin. During the extension period, we observed electron-spin resonance signal from the Curie-law magnetization of the sample's nitroxide molecules at 0.6 tesla and 4.2 kelvin. This success was followed by the observation of nuclear magnetic resonance signal at 0.6 tesla from proton spins whose magnetization has been enhanced by 10 to 20 fold via cross-effect [Maly 2008] dynamic nuclear polarization.

These results represent the first time that microwave-induced dynamic nuclear polarization has been observed in a magnetic resonance force microscope experiment. The results of these experiments were published in April 2016 [Isaac 2016]. The manuscript is 14 pages long and consists of 9 figures, 2 tables, and 58 references. The supporting-information document is 6 pages long and consists of 4 figures, 1 table, and 11 references.

IMAGE RECONSTRUCTION

In Years 2 and 3 we devoted effort to evaluating and improving protocols for reconstructing an image of a sample's subsurface spin density from measurements of spin forces or force gradients as a function of cantilever position. At the start of this work, the state-of-the-art reconstruction method was the iterative Landweber-style algorithm used by the IBM team in their MRFM virus imaging experiment [Degen 2009]. While this algorithm was successful, it took nearly three days of computation time to converge. We succeeded in developing two improved algorithms for reconstructing the proton density of a virus-scale object: a greatly accelerated iterative Landweber-style algorithm and an essentially instantaneous Fourier-based deconvolution stabilized by Tikhonov regularization. We then explored the use of Bayesian-based reconstruction algorithms because they (1) can systematically incorporate sample assumptions such as positive-definite spin density and (2) can in principle produce spin-density error bars along with the reconstructed image. We implemented iterative Bayesian-based reconstruction algorithms using Markov chain Monte Carlo (MCMC) techniques. To date we have succeeded in implementing a Bayesian MCMC reconstruction algorithm for a few-spin system.

CONCLUSIONS

Flipping nuclear spins in solids with high fidelity requires millitesla-amplitude radiofrequecy (rf) magnetic fields. In order to meet the few-milliwatt power budget of a cryogenic magnetic resonance force microscope experiment, we chose to generate the required rf magnetic fields using a microwire [Poggio 2007]. In the Cornell experiment, this microwire was integrated into a coplanar waveguide for operation up to 20 GHz, enabling the observation of nuclear magnetic resonance (NMR), electron spin resonance (ESR), and dynamic nuclear polarization (DNP) in a single experiment for the first time. Aligning a high-compliance cantilever with the micrometer-scale feature of the waveguide at a temperature 4.2 kelvin in vacuum was extremely challenging and took us nearly a year longer than we anticipated. This development time could be reduced by a factor of four or more by purchasing a closed-cycle refrigerator (from, for example, Leiden Cryogenics) with automated, overnight cooling to/from 4.2 kelvin.

Our successful (1) integration of a microwire magnetic field source into a coplanar waveguide and (2) invention of protocols for aligning a high-compliance cantilever operated in the "hangdown" geometry with this microwire should now enable the study of thin film devices prepared on the coplanar waveguide. To minimize sample charging and maintain cantilever force sensitivity near the sample, the sample should be metal coated. Our previous experiments suggest that such a metal coating should improve the surface-related frequency noise experienced by a high-compliance cantilever near a polymer surface [Hickman 2010]. We have already shown that spin signal can be observed with a magnet-tipped cantilever "through" the metal coating [Moore 2009].

Alexson and coworkers have shown that a high-compliance magnet-tipped cantilever can be used in an MRFM experiment to observe the longitudinal component of the sample's nuclear spin magnetization in real time while the magnetization undergoes spin-lattice relaxation [Alexson 2012, Isaac 2016]. Taken together with the results of this grant, we conclude that MRFM is ready to study the nuclear spin relaxation times of thin-film semiconductor devices at cryogenic temperatures. The sample's relaxation times can be studied as a function of temperature, illumination intensity and wavelength, and applied electric field. The relaxation times can be profiled in one dimension as a function of sample depth with a few-nanometer resolution by varying either the RF frequency or the static magnetic field [Isaac 2016].

Enhancing the nuclear magnetic resonance signal from an organic semiconductor device using DNP requires doping the sample with a stable free radical. For spin-cast samples, this doping step will be straightforward to implement. For thermally-evaporated samples, further work will be required to assess the stability of potential free-radical dopants in vacuum at elevated temperature. The scanned-probe magnetic resonance force microscope developed for this grant can be used without modification to detect NMR, ESR, and DNP in a nitroxide-doped biomolecule sample. Obtaining a three-dimensional image of a biomolecule with 5 nm resolution or better in our apparatus requires the use of an attonewton-sensitivity cantilever with a 100 nm diameter magnetic tip [Longenecker

2012] and DNP operating with an enhancement factor of 10 to 20 [Isaac 2016]. Both of these requirements have been met, but in separate experiments. The further studies that will be required to establish the joint use of small-diameter tips and DNP in a single-molecule MRFM imaging experiment are discussed in detail by Isaac and coworkers in their manuscript [Isaac 2016].

More work is required to implement a rapid and robust MRFM three-dimensional image reconstruction algorithm for a dense sample of spins. The lack of a fast and stable image reconstruction algorithm, and not the available signal-to-noise ratio or hardware, is presently the main impediment to create three dimensional images of spin density in both thin-film devices and isolated biomacromolecule samples. The work done on this grant demonstrates that there is considerable room for invoking improved numerical implementations of existing algorithms and for inventing new image-reconstruction algorithms.

REFERENCES

[Alexson 2012]
D. A. Alexson, S. A. Hickman, J. A. Marohn, and D. D. Smith, Single-shot nuclear magnetization recovery curves with force-gradient detection, *Appl. Phys. Lett.*, **2012**, *101*, 022103, URL http://dx.doi.org/10.1063/1.4730610.

[Degen 2009]
C. L. Degen, M. Poggio, H. J. Mamin, C. T. Rettner, and D. Rugar, Nanoscale magnetic resonance imaging, *Proc. Natl. Acad. Sci. U.S.A.*, **2009**, *106*, 1313 – 1317, URL http://dx.doi.org/10.1073/pnas.0812068106.

[Hickman 2010]
S. A. Hickman, E. W. Moore, S.-G. Lee, J. G. Longenecker, S. J. Wright, L. E. Harrell, and J. A. Marohn, Batch-fabrication of cantilevered magnets on attonewton-sensitivity mechanical oscillators for scanned-probe nanoscale magnetic resonance imaging, *ACS Nano*, **2010**, *4*, 7141 – 7150, URL http://dx.doi.org/10.1021/nn101577t.

[Isaac 2016]
C. E. Isaac, C. M. Gleave, P. T. Nasr, H. L. Nguyen, E. A. Curley, J. L. Yoder, E. W. Moore, L. Chen, and J. A. Marohn, Dynamic nuclear polarization in a magnetic resonance force microscope experiment, *Phys. Chem. Chem. Phys.*, **2016**, *18*, 8806 – 8819, URL http://dx.doi.org/10.1039/C6CP00084C.

[Longenecker 2011]
J. G. Longenecker, E. W. Moore, and J. A. Marohn, Rapid serial prototyping of magnet-tipped attonewton-sensitivity cantilevers by focused ion beam manipulation, *J. Vac. Sci. Technol. B*, **2011**, *29*, 032001, URL http://dx.doi.org/10.1116/1.3581102.

[Longenecker 2012]
J. G. Longenecker, H. J. Mamin, A. W. Senko, L. Chen, C. T. Rettner, D. Rugar, and J. A. Marohn, High-gradient nanomagnets on cantilevers for sensitive de-

tection of nuclear magnetic resonance, *ACS Nano*, **2012**, *6*, 9637 – 9645, URL http://dx.doi.org/10.1021/nn3030628.

[Maly 2008]
T. Maly, G. T. Debelouchina, V. S. Bajaj, K.-N. Hu, C.-G. Joo, M. L. Mak-Jurkauskas, J. R. Sirigiri, P. C. A. van der Wel, J. Herzfeld, R. J. Temkin, and R. G. Griffin, Dynamic nuclear polarization at high magnetic fields, *J. Chem. Phys.*, **2008**, *128*, 052211, URL http://dx.doi.org/10.1063/1.2833582.

[Moore 2009]
E. W. Moore, S.-G. Lee, S. A. Hickman, S. J. Wright, L. E. Harrell, P. P. Borbat, J. H. Freed, and J. A. Marohn, Scanned-probe detection of electron spin resonance from a nitroxide spin probe, *Proc. Natl. Acad. Sci. U.S.A.*, **2009**, *106*, 22251 – 22256, URL http://dx.doi.org/10.1073/pnas.0908120106.

[Poggio 2007]
M. Poggio, C. L. Degen, C. T. Rettner, H. J. Mamin, and D. Rugar, Nuclear magnetic resonance force microscopy with a microwire rf source, *Appl. Phys. Lett.*, **2007**, *90*, 263111, URL http://dx.doi.org/10.1063/1.2752536.

Copies of technical reports

Two technical reports were produced by this grant:

1. C. E. Isaac, C. M. Gleave, P. T. Nasr, H. L. Nguyen, E. A. Curley, J. L. Yoder, E. W. Moore, L. Chen, and J. A. Marohn, Dynamic nuclear polarization in a magnetic resonance force microscope experiment, *Phys. Chem. Chem. Phys.*, **2016**, *18*, 8806 – 8819, URL http://dx.doi.org/10.1039/C6CP00084C.

2. J. G. Longenecker *High-Gradient Nanomagnet-on-Cantilever Fabrication for Scanned Probe Detection of Magnetic Resonance* PhD thesis, Cornell University, Ithaca, New York, **2013**, URL http://hdl.handle.net/1813/33775.