Contract Information

<table>
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<tr>
<th>Contract Number</th>
<th>HR0011-04-1-0029</th>
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<tr>
<td>Title of Research</td>
<td>Spintronic Nanodevices Defined by Nanolithography</td>
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<tr>
<td>Principal Investigator</td>
<td>Dr. Charles J. O'Connor</td>
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<tr>
<td>Organization</td>
<td>University of New Orleans, New Orleans, LA 70148</td>
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FINAL TECHNICAL REPORT – December 15, 2007

Purpose:

The purpose of this report is to document the results of the complete effort for this project, which was to explore the possibilities of employing nanoparticles, nanostructured thin films, and nanowires in spintronic nanodevice fabrication by using e-beam lithography techniques at AMRI-UNO.

Progress Summary

(1) Nanotransistors Defined through E-beam Nanolithography – Dr. Weilie Zhou

Our group has been focused on two directions during this project: one is semiconductor nanowires synthesis and one is nanotransistors fabrication using e-beam nanolithography. During the project period, we have been working on semiconductor nanowire synthesis, such as ZnO, SnO$_2$, In$_2$O$_3$, etc. and diluted magnetic semiconductor nanowire synthesis, such as Mn doped and Co doped ZnO nanostructures. Chemical vapor deposition and pulsed laser deposition have been set up by using this DARPA fund. A detailed nanostructure study has been investigated to study the synthesis condition and growth mechanism by XRD, SEM and TEM analysis. Physical properties, such as transport and magnetic measurements, have been performed to investigate the room and low temperature ferromagnetic properties. Detailed writing parameters of nanolithography, such as dose density, exposure time, size, features, photoresist, developing condition, lift-off, etc. have been studied and a solid data base for nanolithography patterning at AMRI has been established. Furthermore, diodes, field effect transistors, mechanic nanodevices have been successfully fabricated using e-beam nanolithography techniques. Spintronic nanotransistors based on nanowires are still under investigation. The nanodevices fabricated in our group can be used in chemical and biological nanosensors, NEMS, spintronics, and photovoltaic devices.

Publications

2. "Characterization of Diluted Magnetic Semiconductors of Co-doped and (FeCo)-
codoped ZnO Nanostructures by Nanoprobe EDS Analysis", J. J. Chen, Y. Yan,
A. West, J. J. Liu, and W. L. Zhou, Microscopy & Microanalysis 13 (Supp.)
737CD (2007).
3. "Fe-doped ZnO Nanowire Arrays Synthesized by Chemical Vapor Deposition", K.
Wang, J.J. Chen, and W.L. Zhou, Microscopy & Microanalysis 13 (Supp.) 736CD
(2007).
4. "Nanostructure and EELS Characterization of Diluted Magnetic Semiconductor
Zn1-xCoxO Nanoneedles", W.L. Zhou, J.J. Chen, K. Sun, and L.M. Wang,
5. "Patterned Metal Nanowire Arrays from Photolithographically-Modified
7. "Fabrication of Mn Doped ZnO Diluted Magnetic Semiconductor Nanostructures
8. "Well-aligned Mn-doped ZnO Nanowires Synthesized by a Chemical Vapor
172505 (2005).
9. "Room-temperature Ferromagnetic Co-doped ZnO Nanoneedle Array Prepared
10."ZnO Nanostructures Fabricated through a Double Tube Vapor Phase Transport
11.Giant Negative Magnetoresistance of Spin Polarons in Magnetic
Semiconductors-Chromium-doped Ti2O3 Thin Films, Z.Wang, Y. Hong, J. Tang,
12."E-beam Nanolithographically Patterned Metal Oxide Nanowire Arrays for Highly
Sensitive Gas Sensors" L. Campbell A. D., D. Smith, G. May, L. Caliste, Y. Chen,
13."Electron Transport Property Measurement of Metal Oxide Nanowire Based
Nanodevices Using Nanomanipulators In-Situ FESEM", Weilie L. Zhou, Mo Zhu


Published book chapters


Presentations


5. “Nanowire Based Electromechanical Switch” Renhai Long, Jiajun Chen, and
Weilie Zhou, Res. Soc. Fall Meeting, Boston, MA, Nov.27 - Dec.01, 2006
17. "E-beam Nanolithographically Patterned Metal Oxide Nanowire Arrays for Highly


Participants
1. Dr. Chen Chen
2. Dr. Mo Zhu
3. Dr. Yuxi Chen
4. Dr. Minhui Yu
5. Mr. Jiajun Chen
6. Ms. Raven Anglin
7. Ms. Jingjing Liu

(2) MAGNETO-OPTICS OF NANOMAGNETIC MATERIALS – Dr. Kevin Stokes

SCOPE

This project explored the integration of chemically-synthesized nanoparticles and nanowires with planar nanostructures defined by electron-beam (e-beam) nanolithography. In addition optical, magnetic and magnetic-optical properties of the structures were investigated to assess the possibility of using such structures as photonic device components. The research included the participation of IBM T.J. Watson Research Center through principle investigator Chris Murray and a post-doc to bridge the research efforts between UNO and IBM.
The primary objectives were to create a process for producing thin films using chemically-synthesized nanoparticles; to pattern this films with electron-beam nanolithography; investigate the magnetic and magneto-optical properties of the nanoparticle assemblies.

MAJOR ACCOMPLISHMENTS

- Demonstrated nanometer-scale patterning of a magnetic nanoparticle film. Films of magnetite (Fe₃O₄) nanoparticles were fabricated using electric-field assisted layer-by-layer assembly with a transparent polyelectrolyte. Produced features down to 50 nm using electron-beam lithography.
- Completed a study of the magneto-optics of closely spaced nanoparticles. Identified novel near-field interaction effects (as a function of interparticle distance) in the magneto-optical response.
- Developed a theory of the near-field optical interactions in nanoparticles to account for the observed magneto-optical response. Theory includes a redefinition of Faraday rotation applicable to scattering from nanostructures and predicts spectrally-specific enhancements for coupled noble-metal/magnetic nanoparticle assemblies which depend on nanometer-scale geometries.
- Successfully synthesized cobalt ferrite nanoparticles with varying cobalt concentration and characterized the magneto-optical response of the nanoparticles.
- Data collected contributed to the funded NSF Grant Novel Chiral Architectures of Magnetic Nanowires, Lead PI: L. Malkinski and Co-PI: K.L. Stokes. The experimental data and theory were also used in the DoD EPSCoR proposals Advanced Magnetic Nanocomposites for Wireless Communications and Optoelectronic Applications (2006) and Chiral Nanowire Composites as Negative Index Materials (2007) and the National Science Foundation proposals Magneto-Optics of Coupled Nanomagnetic-Noble Metal Structures (2005) and Magneto-optical Effects in Coupled Nanometer-Scale Structures (2004).

RESULTS

Master's Degrees Earned


Papers Published (direct result of this funding)


Presentations

"Magneto-Optical Study of Cobalt Ferrite Nanoparticles,” B.L. Scott and K.L. Stokes, to be presented at the 2008 TMS Annual Meeting & Exhibition, New Orleans, LA.


PARTICIPANTS

The following people have contributed to this project.

Dr. Kevin L. Stokes, Co-principle investigator
Damon Smith, Graduate Student
Byron L. Scott, Graduate Student
Jeff Anderson, High-school teacher/graduate student
Dr. William Green, Post-doctoral Research Associate, IBM T. J. Watson Research Center

(3) Developing Nanotechnology of Magnetoerisistive Structures for Spintronic Devices – Dr. Leszek Malkinski

Contributors:

Dr. Leszek Malkinski (head of the group)
Dr. Andriy Vovk (postdoctoral researcher)
Donald Scherer II (graduate student)
Project Goals and Objectives:

To develop materials and nanolithographic techniques to fabricate magnetoresistive structures for nanoscale devices. The structures of interest include giant magnetoresistive and spin tunneling structures. Also, an important part of the project was to establish measuring techniques to measure spin-dependent transport in nanostructures.

Realization of the Project and Results:

A measuring system has been designed and built at AMRI to investigate magnetoresistance of the spin-tunneling junctions with submicrometer dimensions. Precise measurements of magneto-transport properties of nanostructures usually require complex multistep lithographic processes to fabricate electrical leads to the nanostructure. A more convenient solution was proposed which minimizes number of elaborate lithographic processes and essentially eliminates the electric leads. The tunneling junctions can be fabricated in the form of nanosized pillars. Because of small area of the tunneling junction its resistance was estimated to be in the range from hundreds to thousands of ohms. Because the resistance of the leads is typically a fraction of ohm it makes possible to measure the resistance of the junctions using two-probe (or two point) method. Existing atomic force microscope was modified to enable this kind of measurements. The semiconducting AFM tip was replaced by a conductive one and the conductive cantilever was replaced. The conductive atomic force microscope with external electronic instruments was able to find nanoscale objects, make a contact with them, provide a bias and measure the current flowing through the object. Phase-sensitive measurements with two lock-in amplifiers replaced originally proposed DC current measurements in order to improve the signal to noise ratio. The works on the measuring system resulted in Masters in Applied Physics degree of the graduate student supported through this grant.

The theoretical works of W. Butler et al. predicted large tunneling magnetoresistance effect in tunneling junctions with MgO barrier. Initial experimental results reported S. Parkin’s and S. Yuasa’s groups demonstrated that, indeed, the TMR effect in the micron size junctions exceeds the best results (in the junction with alumina barriers) by a factor of two. We expected that reduced size of the junctions should further increase this effect because of smaller number of defects in the small-area barrier.

In addition to physical deposition techniques, such as magnetron sputtering, patterning of the nanopillars was a crucial part of the fabrication process. The patterning of magnetic films was done by the means of the field emission scanning electron microscope with an electron beam writer. Various patterns in the form of magnetic dots, stripes and perforated films have been fabricated by electron beam writing followed by the lift off technique. The size of the smallest structures was 100 nm. Examples of the structures are presented in Figure 1.
Magnetization processes in such structures at quasi-static conditions and at high frequencies (in microwave range) have been carried out using SQUID magnetometer (Quantum Design) and the ferromagnetic resonance system (Brucker EPS system). The shape anisotropy of the patterned objects as well as interactions among neighboring objects in the arrays were both found significant for the switching fields of the tunneling junctions. Improved quality of the junctions could be achieved by replacing the lift-off technique by the ion milling, which or other dry etching process. The ion milling system available at CAMD - LSU, has experienced damage and has only recently been repaired. This fact delayed the final stage of fabrication of the junctions. The efforts to do competitive research in this area will be enhanced by the new system for ion milling funded by Louisiana Board of Regents grant. This system will be installed at AMRI cleanroom in the middle of 2008.

Giant magnetoresistance effect was investigated in NiMnGa shape memory alloys. Single crystals of these alloys do not exhibit magnetoresistance, however alloys fabricated by pulsed laser deposition in the form of nanogranular films showed significant magnetoresistance effect (especially at cryogenic temperatures) related to their morphology and complex spin structure.

In the final phase of the project Fe-doped TiO thin films have been fabricated in collaboration with Prof. Jinke Tang from the Department of Physics, UNO. The films showed room temperature ferromagnetism and therefore are suitable for applications in spintronics.

The partial results on the research have been reported in several presentation on national and international conferences on magnetism and were published in several articles listed below.

**List of Relevant Publications**


List of Presentations

(4) Microstructural Investigation of Electrode Materials used in Rechargeable Li-ion Batteries – Dr. Heike Gabrisch

Rechargeable Li-ion batteries serve as power source for applications in many portable electronic devices (cell phones, lap top computers). Their working principle is based on the reversible intercalation of Li-ions in the van-der-Waals gaps into lattice sites of the active material at both electrodes and the shuttle of the Li-ions between the two electrodes during charge and discharge. The storage and removal of Li-ions from the host lattice are accompanied by reversible changes in the crystallographic and electronic structure. Additionally irreversible changes are observed in the lattice of the intercalation compounds with increased cycle life. Those are attributed to the observed capacity loss of the battery.

Our project focuses on the study of electrode materials by Transmission Electron Microscopy (TEM) techniques. This includes the characterization of irreversible changes observed after electrochemical cycling or ageing at elevated temperature in the charged (lithium depleted) state. The use of single crystal diffraction in a TEM overcomes the
difficulty of distinguishing between closely related structures that is met in x-ray diffraction studies. At the same time image information and structural details of different regions within one powder particle are obtained.

We developed a method for the study of lattice parameters in Li$_x$CoO$_2$ compounds by Convergent Beam Electron Diffraction. A potential application of the localized lattice parameter measurement is to monitor lithium gradients within single crystals making use of the lattice extension that accompanies lithium removal from fully lithiated LiCoO$_2$. This project includes the growth and chemical delithiation of single crystalline LiCoO$_2$ as a source of adequate TEM specimen. More application oriented projects were carried out in collaboration with Dr. R. Yazami at the California Institute of Technology. We studied the crystallographic changes in commercial LiCoO$_2$ and Li$_2$Mn$_2$O$_4$ cathodes after ageing at elevated temperatures. In the aged particles we identified i. the formation of a cubic spinel phase on LiCoO$_2$ particles, ii. a tetrahedral phase on Li$_2$Mn$_2$O$_4$ particles. Both newly formed phases are detrimental for the electrochemical properties of the respective cathodes. In collaboration with Dr. M.M. Doeff at Lawrence Berkeley National Laboratory we investigated carbon coated LiFePO$_4$ particles that are being developed for cathodes in electric and hybrid vehicles. Using Energy Filtered Imaging we proved that the addition of in-situ carbon leads to the formation of a continuous surface film. Investigations of cycled particles showed that the surface films are stable. The repeated lithium insertion and de-intercalation leads to the formation of fractures parallel to low indexed lattice planes. A dislocation-based model can explain the observed fracture surfaces.

Personnel at AMRI supported through this grant: Karin Pruessner, post-doctoral scholar, Qingfeng Xing (postdoctoral scholar, partially supported), Mary Kombolias (grad. student, partially supported), Tanghong Yi (grad. student, partially supported), Fabian Schmitz (visiting grad. student).

Supplemental funding student support was obtained from The Louisiana Board of regents, contract LEQSF(2004-07)-RD-A-36, funding for post doctoral salary was received from the University of New Orleans.

M. Kombolias and Tanghong Yi graduated with a Masters degree doing research for this project.

Conference Contributions


3. "The effect of charge discharge cycling and chemical delithiation on LiFePO$_4"", H. Gabrisch, DARPA UNO/AMRI Review (DARPA Mardi Gras Review), New Orleans,
February 6 2007.


5. "Determination of c lattice parameter in LiCoO\textsubscript{2} by Convergent Beam Electron Diffraction", Q. Xing and H. Gabrisch, 206\textsuperscript{th} Joint International Meeting, 210\textsuperscript{th} Meeting of the Electrochemical Society, Cancun, Mexico, October 29-Novemver 3 2006.

6. "TEM studies of carbon coated LiFePO\textsubscript{4} after charge discharge cycling", H. Gabrisch, J. Wilcox, and M. Doeff, 206\textsuperscript{th} Joint International Meeting, 210\textsuperscript{th} Meeting of the Electrochemical Society, Cancun, Mexico, October 29-Novemver 3 2006. (Invited)

7. "Investigation of Li\textsubscript{x}CoO\textsubscript{2} phases produced by heat treatment of delithiated LiCoO\textsubscript{2} powders", T. Yi, M. Kombolias, H. Gabrisch, 206\textsuperscript{th} Joint International Meeting, 210\textsuperscript{th} Meeting of the Electrochemical Society, Cancun, Mexico, October 29-Novemver 3 2006.

8. "Comparison of carbon coated LiFePO\textsubscript{4} before and after charge discharge cycling" H. Gabrisch, J. Wilcox, and M. Doeff, 7\textsuperscript{th} Louisiana Materials and Emerging Technologies Conference, Baton Rouge, Oct.23-24 2006. (Invited)


10. "Investigation of Li\textsubscript{x}CoO\textsubscript{2} phases produced by heat treatment of delithiated LiCoO\textsubscript{2} powders", T. Yi, M. Kombolias, H. Gabrisch, 7\textsuperscript{th} Louisiana Materials and Emerging Technologies Conference, Baton Rouge, Oct.23-24 2006.


12. "Comparison of lattice parameters in Li\textsubscript{x}CoO\textsubscript{2} compounds obtained from the same parent LiCoO\textsubscript{2} powder", Qingfeng Xing and Heike Gabrisch, DARPA review, New Orleans, July 14 2006.


14. "Distribution of lattice constants in LiCoO\textsubscript{2} measured by CBED" Qingfeng Xing and Heike Gabrisch, DARPA and AMRI review, New Orleans, March 18 2006

15. 208\textsuperscript{th} ECS Meeting,Los Angeles, CA, October 16-21 2005, Rachid Yazami, Yasunori Ozawa, Shu Miao, Brent Fultz and Heike Gabrisch : Isolating the O1 CoO\textsubscript{2} phase

16. 56\textsuperscript{th} Annual Meeting of the International Society of Electrochemistry, Busan,
Korea, September 25-30 2005, H. Gabrisch, Y. Ozawa, R. Yazami, Crystallographic changes in LiCoO$_2$ and LiMn$_2$O$_4$ cathodes observed by TEM after self-discharge at elevated temperatures

17. 3$^{rd}$ ICMAT and 9$^{th}$ International Conference on Advanced Materials (IUMRS-ICAM), Singapore, July 3-5 2005, Karin Pruessner, Heike Gabrisch , Experimental Evidence for a New Ordered Structure in the System Li-Co-O – Electron Diffraction Studies on Cycled and De-Lithiated LiCoO$_2$


19. 207$^{th}$ Meeting of the Electrochemical Society, Quebec City, Canada, May 15-20 2005, H. Gabrisch, Y. Ozawa, R. Yazami, Effect of thermal ageing on the crystal structure of LiCoO$_2$ and LiMn$_2$O$_4$ cathodes for rechargeable Li-ion batteries

20. Joint International Meeting of the Electrochemical Society, Honolulu, Hawaii, October 3-8 2004 , Karin Pruessner, Heike Gabrisch, Rachid Yazami, Phase Transformations during High Voltage Charging of LiCoO$_2$ Cathodes

21. 21rst International Battery Seminar, Primary and Secondary Batteries and Small Fuel Cells, Fort Lauderdale, FL, March 8-11 2004, Karin Pruessner, Heike Gabrisch, Crystallographic Characterization of Cathode Materials for Rechargeable Li-Ion Batteries

22. 204$^{th}$ Meeting of the Electrochemical Society, Orlando, FL, October 12-17 2003. H. Gabrisch, R. Yazami, and B. Fultz, In-situ observations of phase transformations in Li$_{(1-x)}$CoO$_2$ - an electron diffraction study

Publications


6. “Investigation of Li$_x$CoO$_2$ phases produced by heat treatment of delithiated LiCoO$_2$


