

# INTERFACES



The Newsletter of the Center for Materials Research & Analysis at the University of Nebraska-Lincoln

## Facility Focus (I): Multi-purpose X-Ray System

By Brian Jones

A state-of-the-art multi-purpose X-Ray diffractometer(XRD) system is located in the Center for Materials Research and Analysis X-Ray Materials Characterization Facility. The purpose of this acquisition is to support the recently awarded NSF Materials Research Science and Engineering Center (MRSEC) grant, as well as individual investigators at the University of Nebraska by providing new capabilities as well as dramatically increasing research productivity.

The total cost of the system was \$360,000. 70% came from the following funded grant proposal: Acquisition of an X-Ray Diffractometer for Nanoscience Research and Education, submitted to the National Science Foundation’s Major Research Instrumentation (MRI) Program. The remaining 30% was shared by the Center for Materials Research and Analysis, the College of Arts and Sciences, the Department of Physics and Astronomy, and the Office of the Vice Chancellor for Research.

The Bruker-AXS D8 Discover Diffractometer system includes the following highlighted hardware:

- HI-STAR Area Detector
- Centric ¼-Circle Eulerian Cradle
- Laser/Video Sample Alignment System
- Hi-Flux In Plane Hardware
- Goebel Mirror
- V-Groove Ge Crystal Monochromator
- Tilt Stage
- Domed Hot Stage
- Dual Beam Path Analyzer Module

The D8 Discover diffractometer system can be easily reconfigured for the following applications not possible with current instrumentation:

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## From the Director

This issue of Interfaces once again indicates the high level of research activity in materials and nanoscience by our faculty, students and postdocs. I will add to the detailed reports elsewhere a few recent developments of interest.



Our NSF Materials Research Science and Engineering Center (MRSEC) hosted its annual two-day Review and Symposium on September 23 and 24. We benefited from the comments and suggestions of our External Advisory Board including Drs. Bill Gallagher (IBM), Dexin Wang (NVE), Shufeng Zhang (Missouri), Malcolm Stocks (Oak Ridge), and Ron Goldfarb (NIST). The Symposium was entitled “Emerging Challenges in Nanomagnetism,” and featured invited talks by Shouheng Sun (IBM), George Hadjipanayis (Delaware), R. Ramesh (California-Berkeley), Dan Ralph (Cornell), Scott Chambers (PNNL), Sankar Das Sarma (Maryland), and Shan Wang (Stanford). Both events were stimulating and educational.

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# Recent Achievements of Center Researchers

## *Sigma Xi Honors to CMRA Faculty, Staff and Students*

**Reuben D. Rieke** (Chemistry), won the Outstanding Scientist Award for the discovery and development of procedures for preparing active metals, known as “Rieke Metals,” and for investigations of the new chemistry these active metals have made possible.

**Bernard Doudin** (Physics) and **Xiao Cheng Zeng** (Chemistry), were selected for Outstanding Young Scientist Awards. **Doudin** was cited for investigations of the novel magnetic and transport properties of nanostructured nanowires and nanocontacts. **Zeng** was cited for the discovery and investigation of novel forms of water existing within confined spaces and for the discovery of the novel, metal like properties of nanometersized silicon tubes.

**Shelli Krupicka** was selected for the Support of Research Award for her outstanding and efficient work as administrative coordinator for the Center for Materials Research and Analysis.

**Hae-Kyung Jeong** and **Cheol-Soo Yang**, Graduate students in Physics and Astronomy, were selected for Sigma Xi Outstanding Graduate Student Awards.

## *Best Paper Awards*

■ The paper, “Exchange Coupling in P(VDF-TrEE) Copolymer Based All-Organic Composites with Giant Electrostriction,” by **J. Y. Li**, at SPIE 11th Annual International Symposium on Smart Structures & Materials, March 16, 2004, San Diego was selected as best paper in Mechanics and Materials Systems. Physical Review Letter 91, article number 217601.

■ The papers, “Nanomagnetics,” by **R. Skomski**, published in J. Phys.: Condens. Matter 15 No. 4, R109-R142 (2003) and “Spin-Dependent Tunnelling in Magnetic Tunnel Junctions,” by **Evgeny Y. Tsymbal**, published in J. Phys.: Condens. Matter 15 No. 20, R841-R896 (2003) were selected as two of the best papers of 2003 in JPCM.

## *Degree of Doctor Honoris Causa*

**John Woollam** was selected to receive the Degree of Doctor Honoris Causa from Linkoping Institute of Technology at Linkoping University.

## *Recent Patents*

**Bernard Doudin, Cheol-Soo Yang, Andrei Sokolov, Sy-Hwang Liou, Lu Yuan**, “Application of High Spin Polarization Materials in Two Terminal Non-Volatile Bistable Memory Devices,” Patent #6,657,888, 12/2/2003.

**P.A. Dowben**, “Boron-Carbide and Boron Rich Rhombohedral Based Transistors and Tunnel Diodes,” United States Patent 6,600,177, issued July 29, 2003.

**Peter A. Dowben, Shireen Adenwalla, Brian W. Robertson, Mengjun Bai**, “Boron-Carbide Solid State Neutron Detector and Method of Using the Same,” United States Patent 6,771,730, issued August 3, 2004.

**Peter A. Dowben, Anthony N. Caruso, and Yaroslav Losovyj**, “N-Type Boron-Carbide Semiconductor Polytype and Method of Fabricating the Same,” United States Patent 6,774,013, issued August 10, 2004.

**F. Namavar**, “Nanocrystalline, Homometallic, Protective Coatings for Orthopedic Prosthesis,” U.S. Pat. Appl. Publ. 16 pp. CODEN:USXXCOUS2003229399 A1 20031211 CAN 140:19917 AN2003:971784.

**D.J. Sellmyer and C.P. Luo**, “High Anisotropy Perpendicular and Longitudinal Recording Media and Method for Their Preparation,” Patent #6,555,252 B2, Issued 4/29/2003.

## *Paper in Science*

“Spinning Continuous Fibers for Nanotechnology,” by **Yuris Dzenis** was published in Science on June 25; for details see pages 8-9 (an abbreviated version of the published paper).

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Interfaces, the Newsletter of the Center for Materials Research and Analysis, is published periodically. Information, announcements and research updates should be sent to:

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# Zeng Named Guggenheim Fellow

*Reprinted with permission from Scarlet (4/15/04), written by Kelly Bartling*

Xiao Cheng Zeng, Willa Cather Professor of Chemistry, has received a prestigious John Simon Guggenheim Memorial Foundation Fellowship for 2004. The 185 artists, scholars and scientists named in the 2004 United States and Canada competition were selected from more than 3,200 applicants for awards

after earning full professor in 2001.

Zeng said his fellowship will allow for additional time and travel to collaborate with his research partner, Hideki Tanaka of Okayama University in Japan, and other scientists in Asia with whom he has worked on the silicon nanotube research.

“This gives me opportunities to explore more possibilities on this research and travel to collaborate with my partners in Hong Kong, Beijing and elsewhere,” he said.

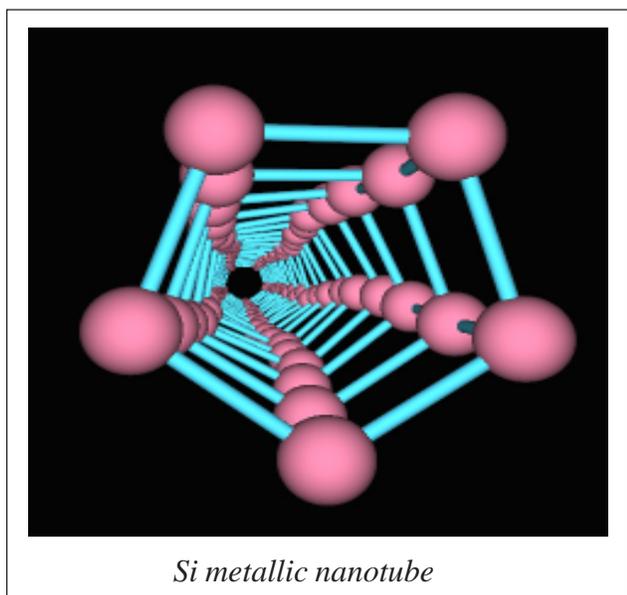
The average Guggenheim fellowship award in 2004 is \$37,362, according to the Guggenheim press release, which feature Zeng’s research among some of its most interesting and unique.

“I am really fortunate to have been selected and singled out,” he said. “I also hope that this reflects well on the University.”

The fellowship is one of several noted in annual Indicators of Quality reports that highlight data, facts and figures for inclusion in various quality reviews. UNL has had only five other Guggenheim fellows since 1962, according to Guggenheim records. Past winners have included Henry Baumgarten, Chemistry; Paul A. Olson, English, 1962; Paul A. Johnsgard, Biological Sciences, 1970; Craig Eckhardt, Chemistry, 1979; and Jim C. H. Wang Chemistry, 2001.

Guggenheim Fellows are appointed based on distinguished achievement and exceptional promise for future accomplishment. What distinguishes the Guggenheim Fellowship program from others is the wide range in interest, age, geography and institutions of those it selects as it considers applications in 79 fields from the natural sciences to the creative arts. Many of these individuals hold appointments in colleges and universities with 87 institutions being represented by one or more Fellows.

Scores of Nobel Laureates, Pulitzer and other prize winners appear on the roll of Fellows, including Ansel Adams, Aaron Copland, Langston Hughes, Henry Kissinger, Vladimir Nabokov, Linus Pauling, Martha Graham, Philip Roth, Derek Walcott, James Watson and Eudora Welty.



totaling \$6.9 million.

Zeng’s fellowship selection is for his research in novel nanostructure of silicon. Zeng in February published a paper on silicon nanotubes in the Proceedings of the National Academy of Sciences. It was his third paper in a major international science journal in three years, two being on low dimensional water and ice, including the discovery of “Nebraska Ice,” in Nature in 2000 and 2001.

Zeng’s research has focused on computational and theoretical studies of liquids, solids, thin films, interfaces, nanotubes and nano-clusters, with further interest in computational nanotribology and modeling of atomic force microscopy.

His UNL appointments are in the Center for Materials Research and Analysis and in the Department of Chemistry. He earned his bachelor’s degree at Peking University and his Ph.D. at Ohio State University. He was hired at UNL in 1993. In 2002, he received the appointment of Willa Cather Distinguished Professor

## Recent Achievements, continued

*continued from page 2*

### *Senior Honors Thesis Advisor Award*

**Susan Hallbeck** was selected as Senior Honors Thesis Advisor for **Jonathan Morse** (Biological Systems Engineering) 2002-2003, and **Lawton Verner** (Biological Systems Engineering) 2002-2003.

### *Student Awards*

The poster of **Anthony Caruso, Andrew Harken, Ellen Day, Shampa Aich** and **Jihee Kim** was selected as one of the best nine out of 91 entries in the Sigma Xi Graduate Student Research Poster Competition, held on Wednesday, 21 April 2004 as part of the UNL Research Fair.

### *National Engineering Conference in Lincoln*

The Department of Engineering Mechanics and College of Engineering, UNL hosted the 41st Technical Conference of the National Society of Engineering Science in Lincoln from Oct. 10-13, 2004. Over 350 papers in all areas of engineering science were presented at the Conference. The Conference was co-Chaired by two CMRA members, Dr. Joseph Turner and Dr. Yuris Dzenis of the EM Department with Dean David Allen serving as Chair. For more info visit: <http://www.nuengr.unl.edu/ses2004/>

The following CMRA-affiliated students have earned their PhDs during 2003 and 2004: **Aliekber Aktag** (Physics, R. D. Kirby), **Jaail Bai** (Physics, X. Zeng), **Tikhon Bykon** (Physics, X. Zeng), **Y. Hu** (Eng. Mech., R. Feng), **H. Huang** (Eng. Mech., R. Feng), **Hae Kyung Jeong** (Physics, P. Dowben), **Alexei P. Leonov** (Chemistry, J.M. Takacs), **Minghao Qin** (Eng. Mech., Y. A. Dzenis), **Steve Schuet** (Chemistry, J. Belot), **Valeriy V. Smirnov** (Chemistry, S. DiMagno), **Yongkui Wen** (Eng. Mech., Y. Dzenis), **Xiangfa Wu** (Eng. Mech., Y. Dzenis), **CheolSoo Yang** (Physics, B. Doudin), **Liyong Yang** (Eng. Mech., J. A. Turner).

The following CMRA-affiliated students have earned their M.S. degrees during 2003 and 2004: **Navid Attarzadeh** (Mech. Eng., B. W. Robertson), **S. Balaz** (Physics, P. Dowben), **Ravi Babu Billa** (College of Engineering, J.I. Brand), **Shicheng Ding (Henry)** (Elect. Eng., R. J. Soukup), **Dangquin Feng** (Physics, P. Dowben), **Goutam Ghoshal** (Eng. Mech., J.A. Turner), **Jianxin Han** (Chemistry, J.M. Takacs), **Yogesh Kane** (Eng. Mech., J.A. Turner), **Dan Liu** (Eng. Mech., J. Li), **Roshanak Nilchiani** (Eng. Mech., J.A. Turner), **Heliang Qu** (Eng. Mech., J. Li), **Vignesh Ramakrishnan** (Elect. Eng., R.J. Soukup), **Sathish Ramamoorthy** (Eng. Mech., J. A. Turner), **Negadip Rao** (Eng. Mech., J. Li), **S. Xue** (Eng. Mech., R. Feng).

**Brad Peterson** (Physics, S. Ducharme) has earned his B.S degree.

## From the Director, continued

*continued from page 1*

Another minisymposium, "Biomedical Applications of Magnetic Nanostructures," was organized by Professor Diandra Leslie-Pelecky and held here on October 8, 2004. The speakers and attendees were treated to the latest research advances in this field that bridges magnetic materials and medicine.

I have been involved with several faculty and administrators from neighboring states in founding the Northcentral States Nanosystems Consortium. A couple of meetings have been held in South and North Dakota with the aim of promoting collaborative research in materials and nanoscience in our region. Several proposals already have been submitted, and a series of web-based research seminars has been initiated.

A large group of Nebraska researchers attended the Magnetism and Magnetic Materials Conference in November, in Jacksonville, Florida. The Nebraska contingent presented 25 papers, one of the largest set from any university at this conference.

I am sad to report the passing of our former colleague, Professor Frank Ullman, of Electrical Engineering. Frank collaborated effectively over many years with Professor John Hardy in Physics, and made many advances in the understanding of ferroelectric materials. Frank and his wife Deb had lived in California for several years, near one of their daughters.

Another transition is that of Dr. Joanna Clark, who was our Materials Specialist in the CMRA Crystallography Central Facility. Joanna now has two small children who need more of her attention. Her contributions will be missed.

Recently the NU Administration requested progress reports on centers and programs supported by the Nebraska Research Initiative. Thus I prepared and submitted reports on CMRA, Nanoscale Materials for Information Technologies, Quantum Information Technology, and Nanoscience for Energy Technologies. Involved faculty have made impressive progress including obtaining about \$82.5 million in external research support since 1988, about 40 patents (about 1/3 of the university total in the past four years), and growth in external support from about \$1 million per year to \$8 million per year. Our faculty should be gratified by their achievements.

Finally, CMRA administers the Nanoscale Science and Technology Program of Excellence supported by special funding from the University. I am pleased to report that seven of the eleven faculty hires have been completed and a search is underway for the eighth this year. We welcome the three most recent hires, Professor Ravi Saraf in Chemical Engineering, and Professors Wonyoung Choe and Barry Cheung in Chemistry. We are most grateful for the strong support of our research programs by the university administration at all levels.

*David J. Sellmyer*

# Facility Focus, continued

continued from page 1

- Grazing Incidence In-Plane XRD (GIIXD)
- Grazing Incidence XRD (GIXD)
- X-Ray Reflectivity (XRR)
- High-Temperature, Orientation Sensitive XRD
- High-Resolution XRD (HRXRD)
- Texture (Pole Figures)
- Residual Stress
- Microdiffraction and Capillary Diffraction

Now this multi-purpose X-Ray system has been put into use.

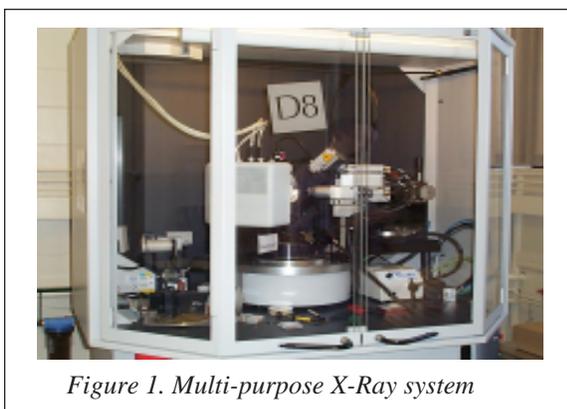


Figure 1. Multi-purpose X-Ray system

## Facility Focus(II): Equipment Upgrade in Electron Microscopy

By Xingzhong Li & Brian W. Robertson

Composition analysis of materials in CMRA's electron microscopes has been greatly enhanced by the addition of the latest digital signal processors, computers, and software, purchased with ONR funds from iXRF, Inc., to the X-Ray detectors on both the SEM and the TEM.

In the case of traditional analog signal processing, the preamplifier output signal is further processed in the main amplifier to obtain the proper pulse amplitude and shape. The output of the amplifier is digitized with an analog-to-digital converter (ADC) and fed into a host computer for processing and display.

In the digital system, all processing is done within the digital module. Once the preamplifier signal is digitized, all further manipulation of the signal is linear and

noise free. Digital filtering is precise and reproducible compared with the non-ideal behavior associated with analog components and finite tolerance. Moreover, digital filtering is not constrained to those filter shapes realizable with physical components, therefore, pulses are resolved better in time and amplitude to give improved throughput, greater light element sensitivity, and lower detectability.

The new system attached to the JSM 840A SEM (see Figure 2) provides vastly improved X-Ray spectrum acquisition from individual locations, lines and areas of samples. In addition, use of the new system with the SEM allows researchers easily to obtain composition profiles and elemental and material phase maps and simultaneous digital images – all from a Windows XP environment that makes data processing, archiving, and electronic file transfer by e-mail, ftp or web transfer straightforward.

The new system on the JEM2010 TEM will allow better, more readily quantified data to be acquired, especially for the lightest elements – down to atomic number 4. At small cost, this system could be further upgraded for line profiling of elemental composition, across interfaces for example.



Figure 2. The new system attached to the JSM 840A SEM.

## CMRA Welcomes Fereydoon Namavar -- By Claudia Reinhardt

As director of Nano-Biotechnology at the University of Nebraska Medical Center (UNMC) and a professor in the Department of Orthopaedic Surgery and Rehabilitation, Dr. Fereydoon Namavar takes a broad perspective on the world's tiniest particles. He is using nano-technology to solve some "big" biomedical problems. Dr. Namavar is developing new nanostructure materials and diagnostic techniques for in vitro and in vivo applications to maximize the lifetime of orthopaedic



Dr. Fereydoon Namavar

implants and minimize the need for revision surgery.

More than 500,000 joint replacement surgeries are performed in North America each year. The procedure involves implanting a prosthesis with two interfacing surfaces, one a metal alloy and the other plastic. Joint replacement is a remarkably successful procedure that restores mobility to patients suffering from arthritis or injury, but the devices aren't always durable enough for active patients or heavier patients. And because people are living longer, they often face a second replacement surgery. These "revision" surgeries can be more painful, more expensive and less successful than the original surgery.

"If the nanocrystalline superhard coatings we are developing can reduce wear in orthopaedic implants and extend the life of the prosthesis, we could eliminate much patient suffering and save health care dollars," says Dr. Namavar. In addition, these nanocrystalline coatings have the potential for even broader biomedical applications. "This technology could help control bone growth through surface design, provide infection-resistant coatings for orthopaedic and dental implants, and much more," he says.

Before coming to the UNMC in 2002, Dr. Namavar was senior scientist and director of Nanotechnology at Spire Biomedical in Massachusetts where he developed various super-hard, wear-resistant coatings to increase the lifetime of bearing surfaces. His research at Spire Biomedical had a wide range of applications, ranging from geothermal drill bits to ortho-

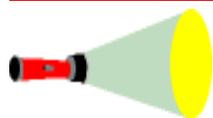
paedic artificial implants. As a manager of Advanced Si-Based Technology for Spire's Optoelectronics he worked on fabrication of components for optoelectronics integration of Si systems. In 1992 he led a group that developed one of the first (nanocrystalline) Si-based visible heterojunction LED's.

A native of Iran, he earned a B.Sc. degree in physics from Tehran University and later studied in England. He earned a Doctor of Science degree with summa cum laude in nuclear physics and did research at the Institute for Nuclear and Radiation Physics at the Katholieke Universiteit Leuven in Belgium. His broad scientific experience encompasses nuclear physics, radiation damage, radiation hard electronics materials, high-temperature electronics materials, optoelectronics, waveguides, modulators, optical beamsteering devices, thin films and nanotechnology.

Dr. Namavar's Nano-Biotechnology Laboratory is located in the Scott Technology Transfer and Incubator Center (STC) near the former Ak-Sar-Ben racetrack in Omaha. His team recently purchased an ion beam assisted deposition (IBAD) system which combines physical vapor deposition with concurrent ion beam bombardment in a high vacuum environment. Dr. Namavar's research includes:

- Application of nanotechnology in total joint arthroplasty for: reducing the wear of orthopaedic implants, and controlling the bone growth through material and surface design,
- Development of smart infection-resistant coatings for orthopaedics and dental implants. In vitro and in vivo absolute wear measurements of orthopaedic implants,
- Development of medical imaging technology by non-ionizing radiation.

Some of his accomplishments have been reported in Scientific American ("Holey Silicon," March 1992), The Wall Street Journal, Science, and other publications. His collaborations with scientists around the world have resulted in more than 150 publications and several patents. His personal interests range from gardening and classical music to archeology and history.



## Research Spotlight: Stephen Ducharme

The research of Prof. Ducharme's group is focused on the unique properties of ultrathin ferroelectric films of polyvinylidene fluoride (PVDF) copolymers made by Langmuir-Blodgett (LB) deposition. PVDF is a crystalline polymer similar in structure to Teflon™, but with a large permanent electric polarization, making it a ferroelectric (in analogy with the permanent magnetization of ferromagnetic materials). PVDF is widely used piezoelectric material for acoustic and electromechanical transducers.

The ferroelectric polymer project started a decade ago with two of the most powerful tools of science—coincidence and opportunism. Ducharme and Prof. Vladimir Fridkin of the Institute of Crystallography, Russian Academy of Sciences, Moscow, had just received a grant from the National Science Foundation (NSF) to develop the PVDF copolymers for use in photorefractive nonlinear optics. Meanwhile, Fridkin's associates Kira Verkhovskaya and Alexander Bune, along with Serguei Palto from the LB group of Lev Blinov, decided, against the recommendation of their senior colleagues, to make LB films from these polymers. Now this was a 'bad idea,' because vinylidene fluoride is not a good amphiphile, has a hydrophilic polar component, but no oily hydrophobic component that would stabilize it at the water surface. The results, however, were spectacular.

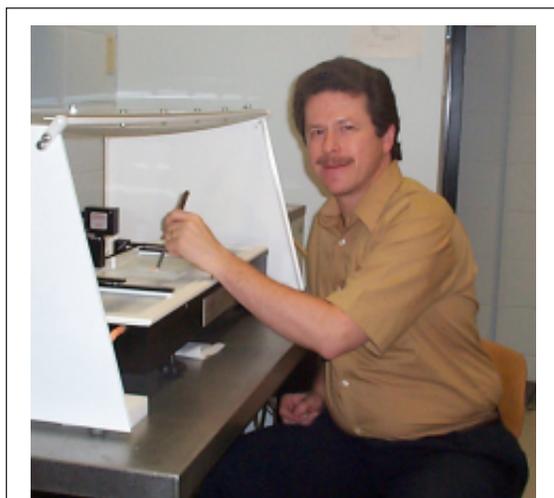
Alexander Bune, Fridkin's PhD student, came to Lincoln in 1995 with some of the first ferroelectric LB films in his pocket. The data from Moscow and Lincoln convinced the three teams that they had something special. Therefore, with the NSF's permission, they immediately abandoned the original plan and dove right in to study the unique ultrathin ferroelectric crystals. Among the discoveries reported by Bune *et al.*, were the discovery of two-dimensional ferroelectricity and the first measurements of the intrinsic ferroelectric coercive field and intrinsic switching dynamics. This work was cited in *Physics Uspekhi* in 1999 as one of 30 "especially important and interesting problems" in physics and astrophysics on the verge of the 21<sup>st</sup> century," by editor V. L. Ginzburg, who had developed the original mean-field theory of ferroelectric with L. D. Landau in 1946.

"Based on my experience and wisdom, I often counsel students and junior colleagues that this measurement is spurious, or that experiment won't work," said Ducharme, "but our most exciting discoveries have proved the contrary." This contrariness was evident in the discov-

eries of Bune, Choi, Borca, and, more recently, Mengjun Bai (PhD 2002). Mengjun showed a mottled-looking atomic force microscope (AFM) image to Ducharme, who pronounced it "junk", some mistake during annealing usually smooth LB films. Bai not only showed that the results were not junk, but that they were natural mesa formations, 10 nm high by 100 nm in diameter, that form spontaneously, by plastic crystalline flow in the paraelectric phase, during annealing of only the thinnest LB films. These 'nanomesas' turned out to be highly crystalline, oriented and ferroelectric, with properties nearly identical to the bulk.

The nanomesas are the basis of novel nanomechanics theories of CMRA member Jiangyu Li (Engineering Mechanics), who has shown that careful structuring of piezoelectric nanocomposites can lead to electromechanical response dramatically higher than any of the individual components. Li shares an NSF nanomanufacturing grant with Ducharme and is joined in the study of nanoscale ferroic composites. Li and Ducharme are joined by John Belot and Takacs, Yongfeng Lu (Electrical Engineering), and Mei, as well as Jerry Bernholc (N. Carolina State) and Simon Phillpot (U. Florida) in several new proposals seeded by a Research Cluster Grant from the UNL Vice Chancellor for Research.

Several other groups joined in to study the properties of these unique films. CMRA member Peter



*Dr. Ducharme is making two-dimensional ferroelectric films with the Langmuir-Blodgett.*

*continued on page 8*

## Research Spotlight: Continued **Spinning Continuous Fibers for Nanotechnology**

-- By Yuris Dzenis

Dowben's group in Physics made several key discoveries of their own—a surface metallicity transition by Jaewu Choi (PhD 1998) and a bulk stiffening transition by Camelia Borca (PhD 2001), and STM imaging and nanoscale polarization manipulation by Jiandi Zhang (a former post-doc) at Florida International University. Neutron and X-ray diffraction studies led by CMRA member Shireen Adenwalla (Physics and Astronomy) have advanced our understanding of the structural transitions (like the stiffening transition), the interplay among polarization, structure, and electric field (Matt Poulsen, BS 2000), and coupling in multilayers (Jihee Kim, PhD candidate). Wai-Ning Mei (UNO Physics) and his group have made considerable progress in ab-initio calculations that compare well with Choi's band-structure studies and Bai's precision IR-VIS-UV ellipsometry studies done in collaboration with the J. A. Woollam Company. Jim Takacs and his group in Chemistry have been synthesizing analogues of PVDF that Poulsen has shown make better LB films, yet remain good ferroelectrics.

Applied research with the ferroelectric polymer LB films includes the demonstration of a working nonvolatile memory element (Tim Reece, MS 2002) and development of a laser imaging technique, scanning pyroelectric microscopy (Brad Peterson, BS 2004). Also critical to the memory applications, Christina Othon's PhD research focuses on the study and control of extrinsic polarization switching.

The CMRA and the Nebraska Research Initiative have been very supportive of the ferroelectric polymer research, enabling many important discoveries and seeding several new projects that are already bearing fruit. The work has been reported widely, in major journals like *Nature*, *Physical Review Letters*, and *Applied Physics Letters*, and at numerous international conferences. External grant funding has been provided by the NSF, the Office of Naval Research, the Air Force Office of Scientific Research, the Petroleum Research Fund, the J. A. Woollam Company, and the Hewlett Packard Corporation.

Ducharme, a native of central Massachusetts, earned a PhD in Physics in 1986 with Jack Feinberg at the University of Southern California. He was an early recruit to the CMRA, joining the faculty in 1991 after two years with IBM, where he and W. E. Moerner (now at Stanford) developed the first photorefractive polymers. Ducharme is now a full Professor and Vice Chair of the UNL Department of Physics and Astronomy.

Nanotubes of carbon and other materials are arguably the most fascinating nanomaterials playing an important role in nanotechnology today. Their unique mechanical, electronic, and other properties are expected to result in revolutionary new materials and devices. However, these nanomaterials, produced mostly by synthetic bottom-up methods, are discontinuous that leads to difficulties with their alignment, assembly, and processing into applications. Partly because of this, and despite considerable effort, a viable CNT-reinforced supernanocomposite is yet to be demonstrated. Advanced continuous fibers produced a revolution in the field of structural materials and composites in the last decades. Fiber properties are known to substantially improve with a decrease in their diameter. However, conventional mechanical fiber spinning techniques cannot produce fibers with diameters smaller than about 2 micrometers. Most commercial fibers are several times that diameter, owing to the trade-offs between the technological and economic factors.

Electrospinning technology enables production of continuous nanofibers from polymer solutions or melts in high electric fields. A thin jet of polymer liquid is ejected, elongated, and accelerated by the electric forces. The jet undergoes a variety of instabilities, dries, and is deposited on a substrate as a random nanofiber mat. There interest in the electrospinning and electrospun nanofibers has been growing steadily since the mid-1990s, triggered by potential applications of nanofibers in the nanotechnology. Over a hundred synthetic and natural polymers were electrospun into fibers with diameters ranging from a few nanometers to micrometers (panel A).

The main advantage of this top-down nanomanufacturing process is its relatively low cost compared to that of most bottom-up methods. The resulting nanofiber samples are often uniform and do not require expensive purification (panels B,C). Unlike submicron-diameter whiskers, nanorods, carbon nanotubes, and nanowires, the electrospun nanofibers are continuous. As a result, this process has unique potential for cost effective electromechanical control of fiber placement and integrated manufacturing of two- and three-dimensional nanofiber assemblies. In addition, the nanofiber continuity may alleviate, at least in part, concerns about the properties of small particles, which have begun to catch the attention of the public [Washington Post, "For Science, Nanotech Poses Big Problems" by Rick Weiss, Sunday, Jan. 31, 2004]. Nanofibers are expected to possess high mechanical properties combined with extreme flexibility. The nanofiber assemblies may feature very high open porosity coupled with remarkable specific surface area. Uses of nanofibers in composites, protective clothing, catalysis, electronics, biomedicine (including tissue engineering, implants, membranes, and drug delivery), filtration, agriculture, and other areas are presently being developed. Clearly there is a growing interest in the pro-

## Spinning Continuous Fibers for Nanotechnology, continued

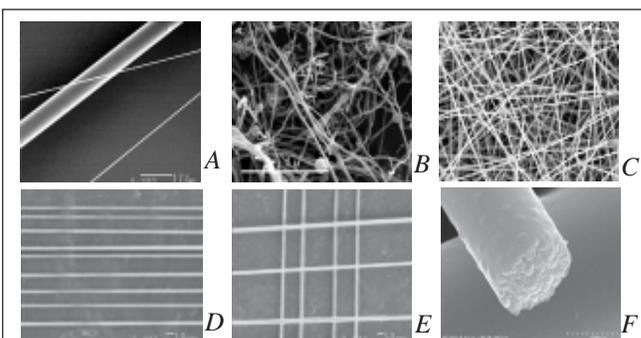
cess, but the results reported to date are centered mostly on the empirical production and the proposed uses of polymer nanofibers. At the same time, thorough understanding of the mechanisms of jet formation and motion is needed for the development of robust methods of process control. Analysis of the electrospinning process is complicated by electromechanical coupling, non-linear rheology, and unusual jet instabilities. Some progress was recently made on modeling of jet initiation. Steady-state spinning was modeled in the non-linear rheologic regime important for polymer jets. Experimental observations and modeling of bending (or whipping) instability produced a major breakthrough in process analysis and understanding. These instabilities are responsible for both rapid jet thinning in this process and the resulting random nanofiber orientation.

More recently, three major breakthroughs were made that are expected to have lasting impact on the quality and scope of the applications. First, several methods of nanofiber alignment were developed that can be roughly classified into methods 'directing' or suppressing jet bending instabilities. The methods need to be further improved because most produce only partial alignment, but the results show promise. Alignment can revolutionize existing and help develop entirely new applications of nanofibers. The modified methods demonstrate the feasibility of integrated nanofiber manufacturing and placement or assembly (panels D,E) that can be extremely economic when compared to the postprocessing methods that are currently being developed for carbon nanotubes. In the second breakthrough, the original process used with high polymers has been modified and applied, in combination with sol-gel chemistry, to produce continuous ceramic nanofibers. These nanofibers can be beneficial in the areas of catalysis, tough and high-temperature ceramics, active and sensing materials, and many others. Nanocrystalline nanofibers such as the one shown in panel F may lead to supertough ceramics. Along with the polymer and polymer-derived carbon and ceramic nanofibers, the sol-gel derived ceramic nanofibers provide a comprehensive nanomaterial and nanomanufacturing platform for extremely broad variety of applications. In the third breakthrough, a method of co-axial electrospinning was developed and used to produce continuous coated and hollow nanofibers. This method allows a single step production of continuous nanotubes or nanopipes that complements the multiple-step template methods of tube production demonstrated earlier.

Despite considerable recent progress, serious challenges remain. Improved models of the process are needed to achieve better understanding of the mechanisms of jet thinning. In particular, thermal and mass transport within the jet in conjunction with solvent evaporation is crucial for jet thinning, solidification, and formation of nanofiber molecular structure. The evaporation leads to inhomogeneous transient concentration and temperature profiles that effect local rheological and other properties of the fluid, and, therefore, jet thinning. The

major experimental challenge is to develop robust methods for manufacturing extremely small nanofibers. Although diameters as small as 3 to 5 nanometers were reported, nanofibers smaller than about 50 nanometers in diameter cannot currently be produced uniformly and repeatedly for most materials systems. The effects of solvent evaporation and jet instabilities on the diameter reduction need to be studied more carefully. Thorough experimental analysis of the composition of the electrospinning instability zone may provide insight on the temporal and spatial evolution of jet instabilities and jet thinning. Another need is to model nanofiber deposition on substrates, both stationary and moving, which can help improve the nanofiber alignment using the newly developed methods and may also lead to the development of novel techniques. Multiple jet electrospinning should also be analyzed and jet interactions with each other as well as with the modified field configurations used in the alignment methods should be characterized and modeled. Multiple jets are critical for the scale-up of the nanofiber production process. New elegant processes yielding high aerial jet densities are expected to be developed. Analysis and implementation of the combined methods involving ultrasmall diameter jets, alignment, and multiple jet spinning are expected to be especially challenging.

Electrospun continuous polymer, carbon, and ceramic nanofibers have considerable advantages when compared to the discontinuous carbon or other nanotubes or nanorods in terms of the cost, health concerns, and the possibility of integrated one-step manufacturing of assemblies. A fundamental experimental and theoretical analysis of the process is needed to develop flexible and reliable methods of fabrication of nanofibers and their assemblies and composites.



**FIGURE** (adapted from the perspective on materials science, Y. Dzenis, *Science*, Vol. 304, 25 June 2004, 1917): (A) Comparison of commercial advanced carbon fiber, one of the smallest advanced fibers available, and electrospun continuous nanofiber. Comparison of (B) vapor grown commercial carbon nanofibers and (C) electrospun carbon nanofibers showing substantially better nanofiber uniformity and sample purity. (D and E) Examples of highly aligned and spaced linear and orthogonal assemblies of continuous nanofibers produced by the gap method of alignment developed by UNL. (F) Cross-section of pioneering continuous nanocrystalline zirconia nanofiber produced at UNL for potential applications in supertough ceramics.



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