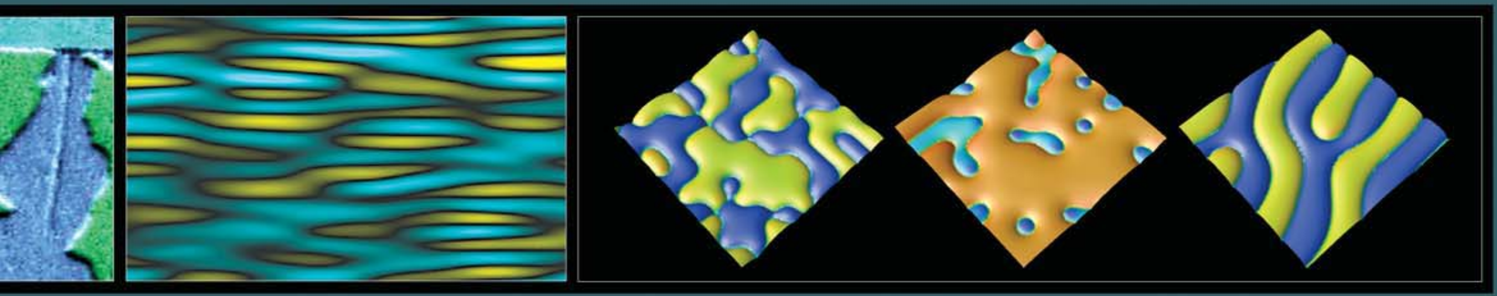
Metallurgy Division



Materials Science and Engineering Laboratory

FY 2002 Programs and Accomplishments

National Institute of
Standards and Technology

Technology Administration

U.S. Department of
Commerce

NISTIR 6907

September 2002

On the Cover:

From the front cover and continuing on to the back, the images shown are, respectively:

Fig 1 - 3-D model of binary eutectic systems under various solidification conditions. (*Dan Lewis*)

Fig 2 - Color representation of one normal mode of magnetization vibration calculated for a 50 nm thick film of Permalloy with 20 nm defects.

Fig 3 - Magneto-optical image of domain patterns in a new "synthetic antiferromagnet" Co/Ru/Co trilayer showing two different types of domains separated by novel non-180 degree walls. Similar trilayers are used in high density recording media.

Fig 4 - Combinatorial pattern of Au/Ni metallization on gallium nitride.

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Materials Science and Engineering Laboratory

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Metallurgy Division

Carol A. Handwerker, Chief

Frank W. Gayle, Deputy

NISTIR 6907

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Executive Summary

This report describes the major technical activities, accomplishments, and areas of scientific expertise in the Metallurgy Division of the NIST Materials Science and Engineering Laboratory in FY2002 (October 2001 through September 2002). In this report, we have tried to provide insight into how our research programs meet the needs of our customers, how the capabilities of the Metallurgy Division are being used to solve problems important to the national economy and the materials metrology infrastructure, and how we interact with our customers to establish new priorities and programs. We welcome feedback and suggestions on how we can better serve the needs of our customers and encourage increasing collaboration to this end.

Mission

Our mission is to provide critical leadership in the development of measurement methods and standards, as well as fundamental understanding of materials behavior needed by U.S. materials users and producers to become or remain competitive in the changing global marketplace. As an essential part of this mission, we are responsible not only for developing new measurement methods with broad applicability across materials classes and industries, but also for working with individual industry groups to develop and integrate measurements, standards, software tools, and evaluated data for specific, technologically important applications.

Establishing Priorities

As part of the development of our technical program, we examine a wide range of research opportunities and make choices for our research portfolio based on several criteria: the match to the NIST mission, the magnitude and immediacy of industrial need, the degree to which NIST's contribution is critical for success, the anticipated impact relative to our investment, our ability to respond in a timely fashion with high-quality output, and the opportunity to advance mission science. This requires that we establish our research priorities through extensive consultation and collaboration with our customers in U.S. industry and with our counterparts in the international metrology community, using a variety of methods including industrial roadmapping activities, workshops, technical meetings, standards committee participation, and individual consultation with our customers.

Within the context of industrial relevance and potential impact of our research, technology trends strongly influence the technical directions addressed by NIST. We prefer to work in rapidly evolving technologies, where advances in measurement science are needed to understand the limitations on system behavior and, therefore, where our contributions are likely to have an impact on the course of technology. For NIST as a whole and the Metallurgy Division in particular, we are committed to having an impact on the measurement and standards infrastructure for the NIST strategic Focus Areas: nanotechnology, health care, homeland security, and information technology/knowledge management. Nanotechnology and information technology/knowledge management are not industry sectors themselves, but are technologies that will have an impact on virtually all present and future industrial enterprises. We have major projects in nanotechnology and homeland security in 2002; additional Division projects will begin in nanotechnology and health care in 2003 and in nanotechnology and information technology/knowledge management in 2004.

Research Portfolio

Our 2002 research portfolio focuses on fulfilling specific measurement needs of the industrial sectors: the magnetic data storage, microelectronics packaging, automotive, aerospace, and optoelectronics industries, and on establishing national traceable hardness standards needed for international trade. Our output consists of a variety of forms, from a fundamental understanding of materials behavior to measurement techniques conveyed through the scientific literature and oral presentations, standard reference materials, evaluated data and online databases, software tools, and sensors for on-line process control.

- **Magnetic Data Storage:** In 2001 we started two new major projects within this program. As part of the National Nanotechnology Initiative, a major collaboration among MSEL, the Information Technology Laboratory (ITL), and the Electronics and Electrical Engineering Laboratory (EEEL) is developing new measurement methods and models for magnetic damping, needed by the magnetic recording industry in the next 3–5 years to improve switching speed. Significant progress has been made in 2002 in modeling and measuring fundamental damping mechanisms through ferromagnetic resonance measurements. In 2002, our long-term project on GMR thin films was refocused into Spintronics, the use of spin-polarized electrons for new devices and magnetic imaging. Through an extensive network of university and industrial collaborators, we are using the process measurement and control capabilities of the MSEL Magnetic Engineering Research Facility to develop an understanding of the materials structure and processing issues in the creation and transfer of spin-polarized electrons.

- **Microelectronics Packaging:** In the MSEL Program on Materials for Microelectronics, we are providing tools for producing improved metal interconnects, from copper on-chip interconnects at the nanometer scale to lead-free solder joints on printed wiring boards. Our project on measurements and modeling of electrodeposited copper for nanometer scale chip interconnection technology continues to produce significant value to the microelectronics community. In the three years since beginning the project, we have developed a measurement technique, a theory for control of interface dynamics, and modeling software for predicting quantitatively the ability of complex electrolytes to fill vias and trenches for on-chip interconnects, and have transferred all of these to the appropriate industrial customers. During the last year, we have demonstrated, in collaboration with International Sematech and Motorola, the generality and versatility of the NIST theory for electrodeposited metals other than copper, and for chemical vapor deposition. In the area of electronics assembly, we continue to play a major role in the NEMI Lead-Free Solder Task Force, with the goal of preparing the U.S. microelectronics industry to assemble products with lead-free solders as required for international trade. In FY2002, the NEMI Lead-free Task Force and NIST have worked together to respond to the needs for critically evaluated data for modeling the reliability of lead-free solder alloys.

- **Automotive:** Within the expanding program on the Forming of Lightweight Materials, we are developing standard test methods for sheet metal forming, measurements of surface roughness, and physically based constitutive laws — and measurement tools needed to reveal them. In FY2002, we have made a major breakthrough in bridging the length scale between dislocation level modeling and macroscopic deformation. This statistical physics approach to propagation of dislocations through dislocation cell walls, and the local accumulation of deformation till slip bands form provides the underpinning for developing physically-based constitutive laws as a function of alloy composition. All of our projects in the Forming of Lightweight Materials Program are done in close collaboration with the automotive industry through formal partnerships, such as USCAR and the Freedom Car, and are designed to help accelerate the design of forming operations for lightweight materials such as aluminum that will ultimately improve fuel economy.

- **Aerospace and Power Generation:** Within the Metals Processing Program, we continue to help U.S. aerospace and power generation industries improve responsiveness and competitiveness by accelerating the design of manufacturing processes for turbine engines. Our development of composition-dependent diffusion mobility databases for superalloy systems provides an efficient method to store a wealth of diffusion data and the means to extrapolate the available data to higher order systems of importance to these industries. NIST collaborates on a DARPA project with General Electric and Howmet Corporation using this approach to accelerate process development for the Ni-Al-Cr-Co-Fe-Hf-Mo-Nb-Re-Ta-Ti-W system.

- **Optoelectronics:** As a result of a growing collaboration between EEEL and MSEL, a Program on Wide Band Gap Semiconductors was established at the end of FY2001 and continued through FY2002. Building on the existing projects on metal interconnects for GaN (Metallurgy Division) and on interface and bulk defects in GaN (Ceramics Division), the EEEL-MSEL program is developing a comprehensive suite of measurement methods for characterizing interface and bulk defects limiting the application of GaN and related materials.

- **National Hardness Standards:** In addition to industry-specific goals, national and international standardization activities are a continuing responsibility. As part of our core NIST mission, we provide national and international leadership in the standardization of Rockwell hardness, the primary test measurement used to determine and specify the mechanical properties of metal products. Our responsibility requires us not only to develop the U.S. national standards with traceability from NIST through NVLAP to secondary standards labs and U.S. metals producers and users, but also to provide leadership to ASTM Standards Committees, the U.S. delegation to ISO, BIPM, and OIML.

Division Structure and Expertise

The Division is composed of 39 scientists, supported by 6 technicians, 6 administrative staff members, and more than 80 guest scientists, and organized into five groups that represent the Division's core expertise in Metallurgical Processing, Electrochemical Processing, Magnetic Materials, Materials Structure and Characterization, and Materials Performance. However, by virtue of the interdisciplinary nature of materials problems in the industrial and metrology sectors that we serve, program teams are assembled across group, division and laboratory boundaries to best meet our project goals. We are committed to assembling the expertise and resources to fulfill our technical goals with the speed and quality necessary to have the desired impact.

Recognition for Division Staff

We are proud of the accomplishments of the Metallurgy Division staff in delivering the measurements, standards, data, and modeling tools needed by our customers. In FY2002, Division members were recognized for the impact and quality of their work by a wide range of organizations, including internally at NIST.

- John Cahn was awarded the 2002 Bower Prize for Achievement in Science for "his unprecedented contributions to the understanding of thermodynamics and kinetics of phase transformations in materials." The award consists of a gold medal and $250,000.
- Daniel Josell, Tom Moffat, and Gery Stafford were awarded the Department of Commerce Gold Medal, the highest honor conferred by the Department, for their pioneering achievements in developing measurement and modeling techniques for controlling copper metallization processes for use in on-chip interconnects. Within two years, they provided the measurement and modeling tools necessary to extend the technology to below 60 nm line width, smaller than the target line width for 2008 according to the 1999 SIA International Technology Roadmap for Semiconductors.
- Ursula Kattner was awarded the NIST Bronze Medal and the ASM George Kimball Burgess Memorial Award for her outstanding achievement in thermodynamics and the application of phase diagrams to important industrial metallurgical processes.
- Bill Boettinger became a NIST Fellow, the highest scientific and technical position at NIST.
- Tom Moffat was awarded the William Blum Award from the National Capital Section of the Electrochemical Society for his research on electrodeposition at the nanoscale and his application of this research to on-chip interconnection.
- Bob Shull was elected as a Senior Member of IEEE.
- Ursula Kattner and Albert Davydov were awarded the 2002 Alloy Phase Diagram International Committee (APDIC) Best Paper award for the best critical review of phase diagram data published in the three years preceding the award.
- Steve Banovic was given the Society of Automotive Engineers Best Paper Award for Wrought Aluminum Alloys for his paper on the effect of microstructural variables on surface roughening in aluminum alloys.
- Chris Johnson was given the International Microelectronics and Packaging Society (IMAPS) Best Paper Award with George Harman of ITL for their paper on "Wire Bonding to Advanced Copper-Low-K Integrated Circuit, the Metal/Dielectric Stacks, and Materials Considerations."
- Jonathan Guyer was awarded the Best Poster Award from the Materials Research Society, 2002 Spring Meeting for his poster on stress-induced instabilities in thin films.
- Carol Handwerker was awarded the SolderTek Award for Lead-Free Solders in recognition of her contributions to lead-free soldering technology in the NCMS Lead-Free Solder Project and in the current NEMI Lead-Free Assembly Project.

Carol A. Handwerker
Chief, Metallurgy Division

Technical Highlights

The following Technical Highlights section includes expanded descriptions of research projects that have broad applicability and impact. These projects generally continue for several years. The results are the product of the efforts of several individuals. The Technical Highlights include:

- Magnetization Dynamics in Films with Nanometer Scale Microstructure
- Ballistic Magnetoresistance: A New Phenomenon with Great Potential for Magnetic Sensors
- Advanced Metallizations for Sub-100 Nanometer Electronics
- Performance-Limiting Defects in GaN
- Responding to the Auto Industry's Research Needs in Materials: Forming of Lightweight Materials
- Thermodynamic Databases for Multicomponent Alloys

Magnetization Dynamics in Films with Nanometer Scale Microstructure

Magnetization damping is essential for data storage and retrieval at GHz data rates in disk drives, MRAM chips and other magnetoelectronic devices. In disk drives, the write head materials, media and read head must all be able to perform well on nanosecond time scales. For measurement of magnetic damping parameters, ferromagnetic resonance (FMR) is the dominant technique, but the raw linewidth data is often clouded by the presence of inhomogeneities. Our modeling of ferromagnetic resonance spectra in inhomogeneous thin films takes a novel approach to a problem that for several decades has been solved only for weak inhomogeneities. Our new model involves solving for the normal modes of an inhomogeneous film and calculating the absorption spectrum from all of the modes. This model provides the theoretical basis for studying the intrinsic damping processes through FMR linewidth measurements, and ultimately for delivering the needed data on magnetic damping to industry.

Magnetic data storage has become the most prevalent form of data storage in the world, far surpassing paper documents in worldwide capacity. Annual hard drive storage capacity shipped is approximately 1×10^{19} bytes with a 60% per year growth rate. To handle anticipated storage at GHz data rates, it is important to understand and control magnetization damping, the process that allows magnetization to come to equilibrium by dissipating heat. To develop high-data-rate hard drives, it will be important to understand and control damping in the magnetic materials used in write heads, media and in read heads. For magnetic random access memory (MRAM) chips, damping is a limiting factor for the speed of these chips because reliable switching of the magnetic "bit" requires waiting for the magnetization to come to equilibrium before the next switching event.

The Nanomagnetodynamics Project is a cooperative project between the Metallurgy Division in MSEL and the Magnetic Technology Division in EEEL. The work is designed to address magnetization dynamics, and magnetization damping in particular, and to deliver to industry the data and metrology needed to develop high-data-rate magnetic devices. This highlight describes a recent theoretical breakthrough by MSEL staff that will enable reliable magnetization damping metrology.

The primary measurement used to determine the damping properties of magnetic materials is ferromagnetic resonance (FMR) linewidth. Ferromagnetic resonance, like electron spin resonance (ESR) and nuclear magnetic resonance (NMR) involves precession of the magnetization around an equilibrium direction at a frequency that depends on the applied field. The damping rate is determined from the width of the susceptibility peak corresponding to the magnetization precession frequency as illustrated in Figure 1.

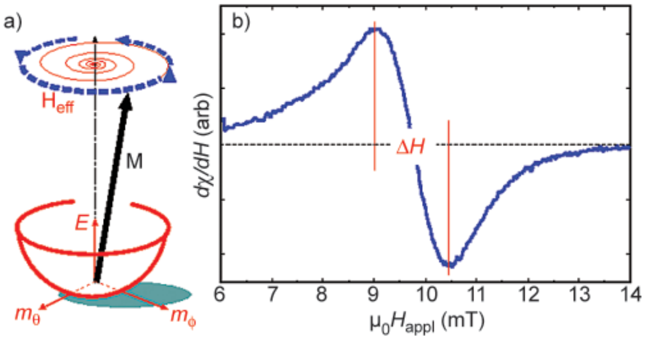


Figure 1. *a) Magnetization precession. Damping causes the magnetization to come to equilibrium as shown by the red spiral. b) A typical FMR signal, taken at 2.5 GHz in a 10 nm thick film of Permalloy. Damping is measured through the line width ΔH.*

Measurements of damping in ferromagnetic materials are complicated by the fact that in addition to damping, inhomogeneity contributes to the FMR linewidth. Reliable interpretation of FMR linewidth data therefore requires separation of the linewidth into components arising from damping and inhomogeneity.

Unlike ESR and NMR in paramagnetic materials, the spins in ferromagnetic materials are strongly coupled by short-range exchange interactions and long range dipolar interactions. To account for magnetic interactions, it is convenient to describe the vibrations of the magnetization in terms of spin waves, or in quantum mechanical language, "magnons." Spin waves (magnons) are the collective vibrational normal modes of the magnetization in a uniform film just as sound waves (phonons) are the collective normal modes of a uniform crystal lattice. The analogy with sound waves is useful in describing the interaction of spin waves with defects. If a sound wave encounters a defect where the elastic properties are different, a portion of the incoming sound energy will be scattered into sound waves traveling in different directions, but with the same frequency. For spin waves, the uniform precession that is driven by a microwave field in an FMR experiment can be scattered into short-wavelength spin waves with the same precession frequency as the uniform mode. The quantum mechanical Hamiltonian describing a system with defects can be written

$$H = \hbar \sum_{\mathbf{k}} \omega_{\mathbf{k}} a^{\dagger}_{\mathbf{k}} a_{\mathbf{k}} + \hbar \sum_{\mathbf{k}} (A_{\mathbf{k},\mathbf{k}'} a^{\dagger}_{\mathbf{k}} a_{\mathbf{k}'} + A^{*}_{\mathbf{k},\mathbf{k}'} a_{\mathbf{k}} a^{\dagger}_{\mathbf{k}'})$$

where $\alpha_{\mathbf{k}}{}^{\dagger}$ and $\alpha_{\mathbf{k}}$ are the magnon (or phonon) creation operators for waves at frequency $\omega_{\mathbf{k}}$ and $A_{\mathbf{k},\mathbf{k}}$ is a coefficient describing the strength of the defect that produces scattering.

The “two-magnon” model was first derived in the 1950’s to describe the effects of defects on linewidth measurements in bulk ferrite materials. Until the present work, it was the most sophisticated model of inhomogeneities in FMR.

The physical picture presented by the two magnon model is that inhomogeneities cause energy to be transferred from the $\mathbf{k} = 0$ uniform precession mode to other $\mathbf{k} \neq 0$ spin wave modes having the same frequency. The two-magnon model is expected to be valid when the spin wave amplitudes are small compared to the uniform precession amplitude, so scattering from spin wave modes back to the uniform precession mode is weak and spin wave−spin wave interactions are not important.

Our approach to the problem of ferromagnetic resonance in inhomogeneous thin films treats the very common case where the $A_{\mathbf{k},\mathbf{k}}$ coefficients are too large for the two-magnon model to be valid. To do this, we start with the Hamiltonian for films with inhomogeneities given above and find the eigenmodes and eigenvalues directly. This process involves constructing a model microstructure of the film, calculating the $A_{\mathbf{k},\mathbf{k}'}$ coefficients, limiting the Hamiltonian to approximately 1000 spin wave modes and computationally diagonalizing the Hamiltonian matrix having elements $A_{\mathbf{k},\mathbf{k}} + \omega_{\mathbf{k}}\delta_{k,k'}$.

The resulting eigenmodes of the inhomogeneous film are mixtures of the spin waves and the uniform, $\mathbf{k} = 0$ precession mode. Each eigenmode has a finite coupling to a uniform driving field that depends on the amount of the $\mathbf{k} = 0$ mode that it contains. Figure 2 shows the eigenmode spectrum and an eigenmode for a typical calculation.

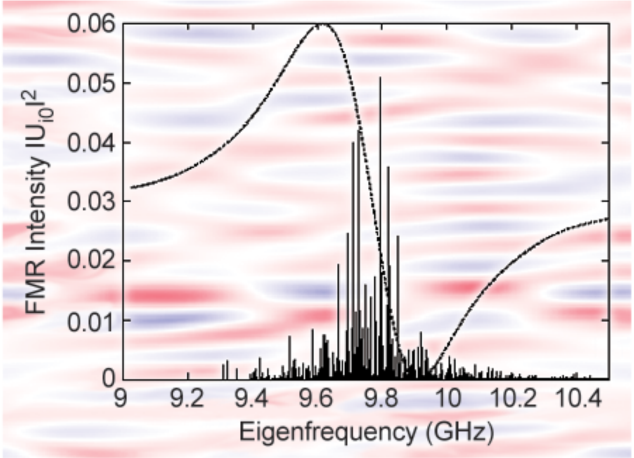


Figure 2: *Eigenmode spectrum of an inhomogeneous thin film. Each eigenmode couples directly to the uniform FMR driving field to give the simulated FMR spectrum shown. The background image is the magnetization pattern corresponding to one of the eigenmodes. The image width is 5 mm and the defect size is 20 nm.*

The physical picture presented by this model is very different from that of the two-magnon model. Inhomogeneities do not merely couple the spin wave modes, they cause mixing of the spin wave modes into a new set of eigenmodes, each of which is observable in an FMR experiment. In this picture, it is clear that the linewidth caused by inhomogeneities is due to a spreading of the FMR intensity in frequency, not to any additional damping process.

Figure 3 shows a comparison between our eigenmode calculation, the two-magnon model and experimental linewidth measurements for a 20 nm film of Permalloy deposited on polycrystalline NiO. The coupling to antiferromagnetic NiO produces an inhomogeneous “exchange bias” field and a uniaxial anisotropy field that varies in strength and direction from grain to grain. These intentionally created “defects” are turned off by deposition of a thin layer of Ta on the NiO, decoupling it from the Permalloy.

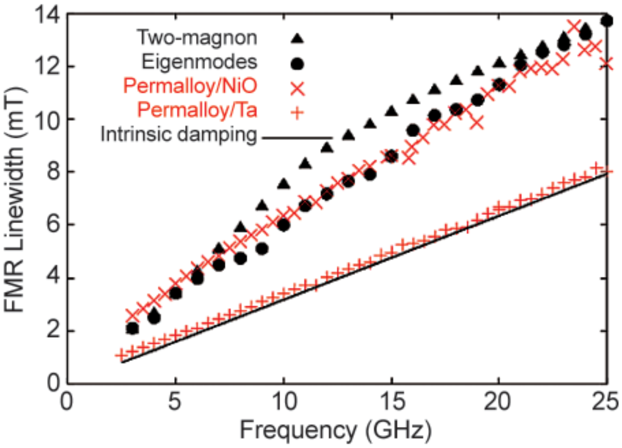


Figure 3: *Comparison of the two-magnon model and the eigenmode model of FMR line width with Permalloy films: one made inhomogeneous by NiO and a control sample.*

The development of this new model of FMR in inhomogeneous films is important in several respects.

- It gives a clear physical picture of the magnetization dynamics in inhomogeneous thin films.
- It clarifies that the linewidth due to inhomogeneities does not constitute a different kind of damping.
- It provides the theoretical basis for interpreting FMR linewidth that will allow us to study the intrinsic damping processes and, ultimately, to deliver the necessary data to industry.

For More Information on this Topic

For further information on magnetization dynamics, damping and ferromagnetic resonance, please contact R.D. McMichael.

Andrew Kunz and R.D. McMichael, “Normal Mode Mixing and Ferromagnetic Resonance Linewidth.” *IEEE Trans. MAG, (in press).*

Ballistic Magnetoresistance: A New Phenomenon with Great Potential for Magnetic Sensors

Magnetic sensors play a central role in many important technologies ranging from data storage to health care to homeland security. A common need among these technologies is higher sensitivity and smaller size. One possible route to higher sensitivity and smaller size is the introduction of the Ballistic Magnetoresistance (BMR) effect as a method of sensing magnetic fields. Although BMR is, at present, a poorly understood and poorly characterized effect, it has shown very large magnetoresistance values in nanoscale devices and could potentially lead to dramatic improvements in magnetic sensors. NIST has initiated a program aimed at clarifying, controlling, and utilizing BMR for advanced magnetic sensor applications.

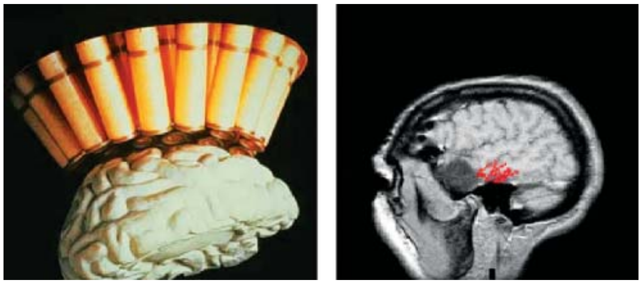
Magnetic sensors play a central role in many important technologies. To name just a few, computer hard disk drives use magnetic sensors to read stored data, magneto-encephalography uses magnetic sensors to image brain wave activity, and bio-hazard detectors use magnetic sensors to detect magnetic beads that are bio-tagged for biological agents such as anthrax, botulism, and cholera.

Figure 1: *Computer hard disk drives use a magnetic sensor to read data.*

A common need among these technologies is sensors with higher sensitivity and smaller size. With higher sensitivity and smaller size, more data could be stored on a hard disk, higher resolution imaging of brain activity would be possible, and earlier warnings of bio-contamination could be given.

The recent discovery of the Ballistic Magnetoresistance effect (BMR) holds the promise of both greatly increased sensitivity and greatly reduced size for magnetic sensors. Figure 3 illustrates how a typical sample is fabricated.

Magneto-encephalography: Imaging Brain Activity


An array of 37 magnetic sensors:

An image of epileptic activity:

Figure 2: *Magnetic sensors are the only technology available for real-time imaging of brain activity. Current sensors are bulky and provide low resolution. Advanced sensors could provide much higher resolution and provide improved surgical guidance.*

A sharp Ni wire is placed about 20 μm from a flat Ni substrate. In an electrochemical cell, an electrodeposition potential is applied between the wire and substrate. A fine column of Ni grows out from the wire until it meets the substrate. When electrical contact is made between the column and the substrate the electrodeposition potential drops immediately to zero and the electrodeposition stops. At the point of contact with the substrate, the column has a diameter of ~10 nm. When the wire and substrate are magnetized in parallel, electrical current easily flows through the nanocontact. However, when the magnetization is antiparallel, as illustrated in Figure 3, electrons tend to be reflected at the nanocontact because they have the wrong spin to pass easily through this region, and a sharp increase in electrical resistance is observed. This effect is known as magnetoresistance, and values as large as 700% have been observed in this type of magnetic nanocontact.

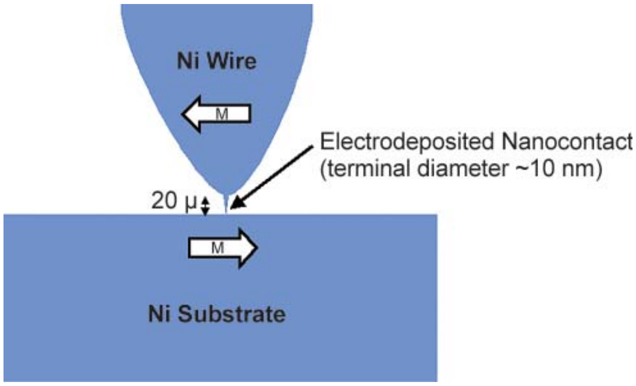


Figure 3: *An illustration of magnetic nanocontacts formed by electrodeposition that exhibit very large values of magnetoresistance (N. García, et. al., 2001).*

To put this result in context, the sensors that read data from hard disk drives currently have a magnetoresistance of only about 15%, almost 50 times smaller. Moreover, the size of the nanocontact in BMR samples is ~50 times smaller than the hard disk drive sensors. Thus, the BMR effect holds the potential for magnetic sensors of greatly increased sensitivity and greatly reduced size.

The term “ballistic” means that the nanocontact is too small for electrons to flip their spin in transit, as they would in a macroscopic Ni sample.

Unfortunately, it often takes many years to go from laboratory demonstration of a concept to a commercially successful device. While BMR looks promising, it is certainly at an early stage of development. The samples investigated so far have poor reproducibility, poor stability, and poor reliability. The techniques of fabrication are poorly understood, and there is no theory that can explain the magnitude of the BMR effect.

Fortunately, there is the precedent of the Giant Magnetoresistance (GMR) effect to serve as a model. When GMR was discovered in 1989, it was subject to very similar shortcomings. Many experts thought it would never be a commercially successful technology. However, the technical community, assisted by a strong effort at NIST, began to address the issues, and gradually the problems were solved. The result is that, today, every hard disk drive produced in the world uses GMR technology in the read head.

Clearly, the sample geometry illustrated in Figure 3 is not suitable for fabrication of hard disk read heads. The industry’s manufacturing practices require lithographic processing on wafers, and a fundamentally different approach would be prohibitively expensive. In light of this need, initial work at NIST has focused on techniques for achieving BMR in planar geometries on wafers. Our first attempt is illustrated in Figure 4. Although the geometry looks ideal, the BMR achieved so far is only 14%. We believe the problem lies in the method of pinhole formation. Consequently, we are exploring novel approaches to controlling pinhole size, such as the use of the Coulomb explosion that occurs when a highly charged ion like Xe^{44+} contacts a surface. By varying the charge on the ion, the size of the pinhole can be finely tuned.

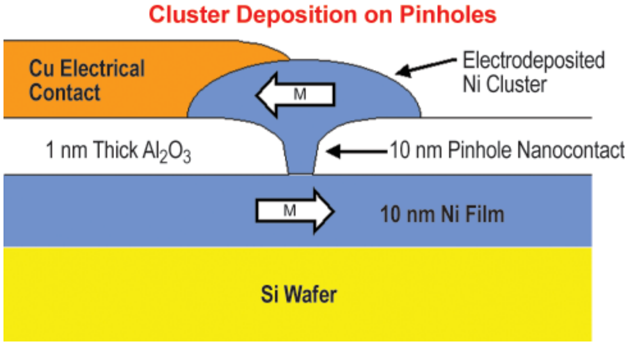


Figure 4: *A planer geometry for BMR. Pinholes are created by dielectric breakdown at thin spots in an Al_2O_3 film when the electrodeposition potential is applied.*

A different and much more successful planar geometry on a wafer is illustrated in Figure 5. In this work, a Ni film ~10 nm thick is deposited on an insulating wafer and patterned into the form of a nano or micro gap. Electrodeposition is used to bridge the gap with a Ni nanocontact. In such samples, we have been able to achieve a much higher BMR value of 350%. However, problems with reproducibility, stability, and reliability remain. We are investigating these shortcomings with scanning electron microscopy (SEM) with polarization analysis, transmission electron microscopy (TEM), Lorentz microscopy, and scanning tunneling microscopy (STEM). The field of BMR is so new that very little microscopy has been carried out to date.

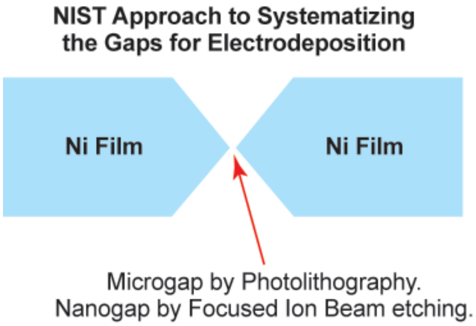


Figure 5: *An illustration of Ni films with lithographically patterned gaps for electrodeposition of magnetic nanocontacts on wafers.*

We believe that with these studies, it is likely that the shortcomings of BMR materials can be addressed, and BMR technology can move towards a new generation of ultrasensitive nanoscale magnetic sensors that will have wide-ranging impact on many important technologies.

> *“The technical challenges facing the data storage industry in the next 10 years are so broad and so deep that the industry cannot do it alone. We need researchers like you here at NIST to help us.”*
>
> ***Dr. Sining Mao***
> Director, Read-Head Research
> Seagate Technology
> June 14, 2002

For More Information on this Topic

Contact: W.F. Egelhoff, Jr.

M. Muñoz, G.G. Qian, N. Karar, H. Cheng, I.G. Saveliev, N. García, T.P. Moffat, P.J. Chen, L. Gan, and W.F. Egelhoff, “Ballistic Magnetoresistance in a Nanocontact between a Ni Cluster and a Magnetic Thin Film.” *Appl. Phys. Lett.*, 79, p. 2946, (2001).

Advanced Metallizations for Sub-100 Nanometer Electronics

Electrodeposited copper is rapidly replacing aluminum in device interconnect technology because of its lower electrical resistivity, superior electromigration behavior, and the ability to fill fine features without the formation of seams or voids. As feature dimensions go below 100 nm difficulties in maintaining performance are anticipated. In FY2002 we have pushed the quantitative limits of the Curvature Enhanced Accelerator Coverage (CEAC) mechanism developed in the Metallurgy Division of NIST. Exploring the mechanism has yielded new electrochemical processing routes for improved metallization and is guiding the development of advanced metallizations beyond copper as well as new processing routes such as surfactant catalyzed chemical vapor deposition.

This Metallurgy Division project is meeting the microelectronics industry's need for improved device metallization by exploring advanced materials and processes for superconformal film growth. In FY2002 we have:

- Established the generality of the CEAC model for superfilling by electrodeposited silver and other metals;
- Developed a new processing method for eliminating the delay time for superfill to begin during electrodeposition, thereby increasing the aspect ratio and decreasing the width of trenches that can be superfilled; and
- Extended the CEAC mechanism to quantitatively predict superfill during chemical vapor deposition.

Our current measurement and modeling effort is focused on copper and silver metallizations, the latter metal having the lowest resistivity of any element, thus having potential on-chip applications. Superconformal silver deposition was demonstrated this year in the Metallurgy Division and is the first example of superconformal feature filling with a metal other than copper. "Superfilling" is characterized by bottom-up deposition as shown in Figure 1.

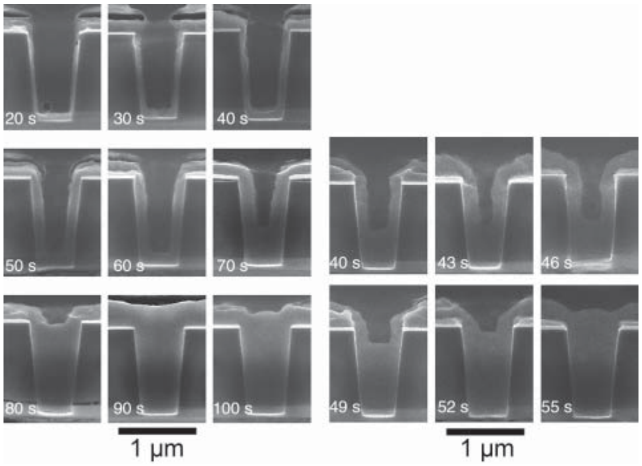


Figure 1: *Superconformal filling of vias during silver (left) and copper (right) electrodeposition (NIST Metallurgy Division, using patterned wafers from International SeMaTech).*

Filling of trenches and vias with silver and copper is quantitatively explained by the Curvature Enhanced Accelerator Coverage Mechanism (CEAC) developed at NIST. Electrochemical and surface analytical measurements on planar substrates were used in FY2002 to establish a one-to-one correlation between catalyst coverage and the metal deposition rate. In the case of silver deposition, adsorbed selenium was found to catalyze the deposition rate. For the thiol/disulfide-polyether-halide additives used in copper superfilling, the sulfonate-end group of the thiol or group of the thiol or disulfide molecules was found to destabilize the passivating polyether surface film thereby accelerating the local metal deposition rate.

The insight provided by uncovering the CEAC mechanism has enabled the development of a new two-step process for superconformal film growth; in contrast to standard electrodeposition techniques, the catalyst is deposited on the substrate prior to the metallization. Specifically, the patterned substrate is first

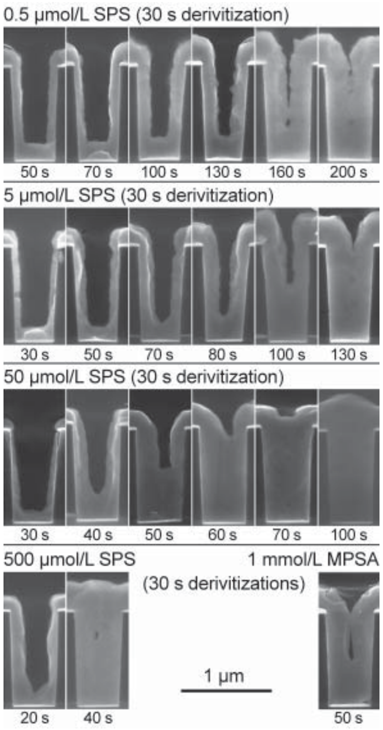


Figure 2: *Time evolution of trench filling after different "derivitization" steps. The concentration of SPS or MPSA catalyst used for the 30 s surface derivitization steps are indicated. All specimens were transferred to a catalyst-free electrolyte for copper deposition.*

"derivitized" or "dosed" with a submonolayer coverage of catalyst and then transferred for electroplating in an electrolyte that does not contain the catalyst. For an optimum catalyst coverage, superconformal filling of trenches and vias occurs as shown in Figure 2 (50 µmol/L SPS). If the catalyst coverage is too low or high, conformal or subconformal deposition occurs, resulting in void formation during feature filling (0.5, 500 µmol/L SPS, 1 mmol/L MPSA). The filling behavior is completely analogous to that obtained using a single (conventional) electrolyte containing both catalytic and inhibiting species. The new process provides unambiguous verification of the CEAC mechanism of superconformal film growth. Restricting the catalyst to the surface prior to metal deposition also enables the rate differentiation provided by the CEAC mechanism to be increased relative to the conventional process. From a technical perspective, the two-step process offers an interesting solution to the difficult control issues associated with catalyst destruction and related aging effects which are known to occur in the "conventional" single-electrolyte superfilling process currently used in industry.

The generality of the CEAC mechanism has now been extended to include the first quantitative prediction of superconformal chemical vapor deposition (CVD). More recently, this work has enabled a direct comparison of the CEAC mechanism with detailed experiment results on iodine catalyzed copper CVD as shown in Figure 3.

Project results from FY2002 have firmly established the generality of the Curvature Enhanced Accelerator Coverage (CEAC) mechanism, which we developed in FY2001 to explain superconformal electrodeposition of copper. The output also clearly demonstrates the predictive power of the CEAC formalism.

Three different electrode-shape change algorithms have been developed. They show excellent agreement with experimental results.

These algorithms, in the form of software, are available from the Metallurgy Division website and are currently being examined by Texas Instruments and IMEC. In addition, Motorola (B. Melnick and M. Freeman), International SeMaTech (C. Witt) and Hynix Semiconductor (S.G. Pyo) are now active collaborators in our experimental and modeling efforts. The first two provide patterned wafers for NIST electrodeposition studies; the last provides results from iodine catalyzed chemical vapor deposition experiments for NIST modeling.

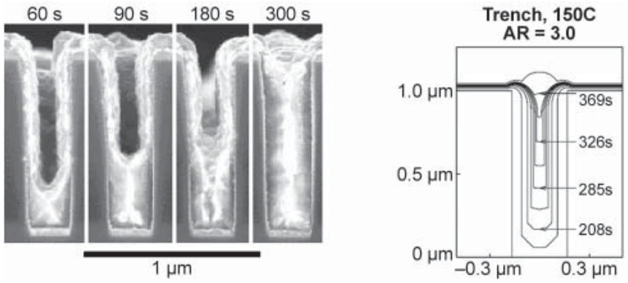


Figure 3: *Superconformal filling of vias during iodine catalyzed chemical vapor deposition. Experimental via results are from Hynix Semiconductor, and model predictions for a trench are from the Metallurgy Division of NIST.*

Selected Project Publications for FY2002

D. Wheeler, D. Josell and T.P. Moffat, Modeling Superconformal Electrodeposition Using the Level Set Method, J. Electrochem. Soc., submitted July 2002.

T.P. Moffat, D. Wheeler, C. Witt and D. Josell, Superconformal Electrodeposition Using Derivitized Substrates, Electrochemical and Solid-State Letters, submitted May 2002.

D. Josell, S. Kim, D. Wheeler, T.P. Moffat, S.G. Pyo, Superconformal Deposition by Iodine-Catalyzed Chemical Vapor Deposition, J. Electrochem Soc., submitted May 2002.

B.C. Baker, M. Freeman, B. Melnick, D. Wheeler, D. Josell, T.P. Moffat, Superconformal Electrodeposition of Silver from a KAg(CN)2-KCN-KseCN Electrolyte, J. Electrochem. Soc., in press.

D. Josell, B. Baker, C. Witt, D. Wheeler and T.P. Moffat, Via Filling by Electrodeposition: Superconformal Silver and Copper and Conformal Nickel, J. Electrochem. Soc., in press.

T.P. Moffat, B. Baker, D. Wheeler, J.E. Bonevich, M. Edelstein, D.R. Kelly, L. Gan, G.R. Stafford, P.J. Chen, W.F. Egelhoff, and D. Josell, Superconformal Electrodeposition of Silver in Submicron Features, J. Electrochem. Soc. 149, C423 (2002).

D. Josell, D. Wheeler and T.P. Moffat, Superconformal Electrodeposition in Vias, Electrochemical and Solid-State Letters 5, C49 (2002).

D. Josell, D. Wheeler and T.P. Moffat, Superconformal Deposition by Surfactant-Catalyzed Chemical Vapor Deposition, Electrochemical and Solid-State Letters 5, C44 (2002).

D. Josell, D. Wheeler, W.H. Huber, J.E. Bonevich and T.P. Moffat, A Simple Equation for Predicting Superconformal Electrodeposition, J. Electrochem. Soc. 148, (12) C767 (2001).

Our findings have also been conveyed to U.S. industry, academia and other national laboratories through more than ten external presentations in the last year.

For More Information on this Topic

D. Josell, D. Wheeler, B. Baker, T.P. Moffat

Performance-Limiting Defects in GaN

The III-V nitrides and GaN, in particular, are emerging new semiconductors for electronic devices, including light-emitting diodes (LED) and laser diodes in the blue-green and UV wavelengths, UV detectors and ultrahigh power switches. The main challenges in this technology are optimization of optical output efficiency and stability of metal contacts. One objective of the MSEL project on GaN is to quantify the effect of GaN defects, in particular of threading dislocations, on these properties. In FY2002 a mechanism for the degradation of electrical contacts through threading dislocation-mediated phase transformations was determined through detailed characterization using transmission electron microscopy. Doping methods to disable the mechanism may lead to greatly improved stability, reliability, and performance of commercial GaN devices.

Direct bandgap GaN and its alloys with AlN and InN are receiving considerable attention as promising semiconductors for electronic devices operating at high temperatures, high frequency and high power and for optoelectronics applications in the blue-green and UV wavelengths. Therefore, electrical contacts to the nitrides (ohmic contacts and Schottky barriers) which are stable at elevated temperatures are needed.

As bulk crystals of these materials are not available, GaN is epitaxially grown on a substrate, usually on (0001) sapphire or (0001) 6H-SiC. Because of a large lattice mismatch between the substrates and GaN, high densities of various crystallographic defects are present in the active GaN layers. Among the defects that can cross the epitaxial GaN layer and reach a surface are threading dislocations, inversion domains, nanopipes and prismatic planar defects.

In order to achieve desirable characteristics of ohmic contacts, different combinations of different metal layers have been studied. For example, the commonly accepted contact to p-type GaN is Ni/Au which gives good electrical characteristics after annealing at 400-600°C. For higher temperatures, the electrical characteristics worsen and severe degradation of contact morphology is observed. Degradation of such electrical contacts are associated with dislocations in GaN, island formation in the contact layers, and decomposition of GaN. In FY2002, NIST developed a mechanism for contact degradation that is based on heterogenerous nucleation of GaN decomposition at threading dislocations/metal interface, followed by wetting of the threading dislocation by liquid Ga. The morphology of the metal/GaN interface is an important issue: if the Ga metal were to penetrate through a thin GaN layer and reach an underlying layer in a device, the device could be rendered inoperable. Furthermore, the stability of interfacial morphology is a general concern for contacts to all semiconductors.

Reaction and interdiffusion in the Au/Ni/GaN system as a function of annealing temperature from 400 to 900°C has been investigated by several groups, mostly using Rutherford backscattering (RBS), Auger spectroscopy and x-ray scattering. Only rarely has this microstructural evolution been directly observed using transmission electron microscopy (TEM). In collaboration with researchers from the Electrical Engineering Department at Howard University, we investigated electrical and microstructural behavior of Ni/Au bilayers as a function of annealing temperature, with emphasis on structural evolution at a TEM level. The as-deposited layers consisted of 50 nm of Ni and 35 nm of Au, with Ni in contact to n-type GaN. Ohmic contacts with a specific contact resistivity, ρ_s, as low as 6.9×10^{-6} Ω-cm^2 for a doping level of 5.0×10^{17} cm^{-3} were obtained after annealing the sample for 10 s at 800°C. Two very important conclusions were achieved from the TEM investigation:

1. A strong reaction between the metal contact layer and the threading dislocations core structure leads to decomposition of GaN along dislocation lines. Such behavior will be a major factor limiting annealing temperature and operation temperature/time of devices.
2. Interdiffusion between Ni and Au results in reversal of Au and Ni phases across the metal film. Thus, after annealing the phase primarily responsible for the formation of the energy barrier of the contact between GaN and metal contact is Au-based.

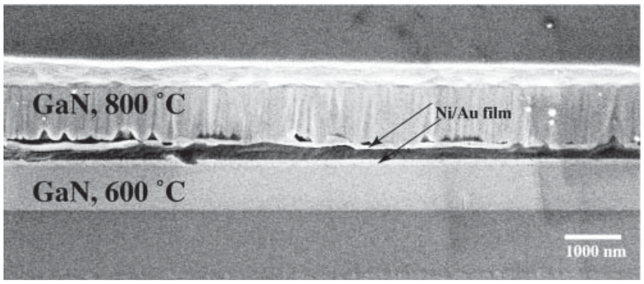


Figure 1: *SEM image of Au/Ni/GaN/sapphire annealed at 600 and 800°C for 10 sec.*

Figure 1 shows a SEM image of Au/Ni/GaN annealed at 600 and 800°C for 10 sec. For the imaging, we used a cross-sectional ion milled TEM specimen where two differently annealed specimens were glued face to face. Whereas at 600°C the metal film is continuous, at 800°C severe degradation of the metal contact occurred. In many places the film is separated from GaN, and deep V-shaped pits can be found penetrating GaN. Such pits are detrimental to the near-surface electrical performance of devices.

TEM analysis of these specimens showed that the V-shaped pits are always associated with the threading dislocations. Figure 2 shows bright and dark field images of the 600°C-annealed specimen. The pits are clearly seen in the bright field image and marked by triangles. The weak beam imaging using different g-vectors established that each pit is connected to a place where a threading dislocation exits GaN. The threading dislocations vary in character (e - edge, s - screw and m - mixed).

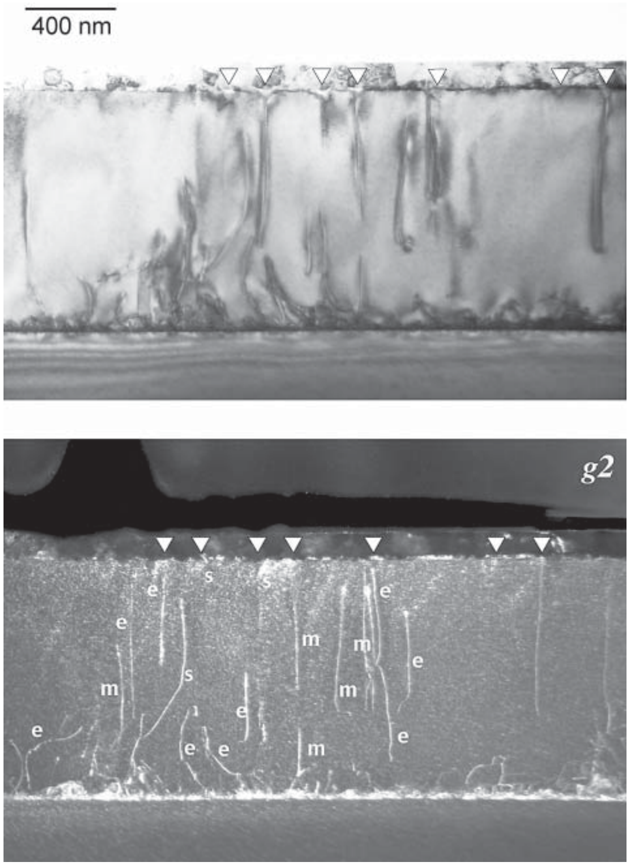


Figure 2: *Bright field (upper) and weak-beam dark field (bottom) images of the 600°C-annealed specimen.*

Bright and dark field images of the 800°C-annealed specimen are shown in Figure 3. The pits associated with the threading dislocations in the specimen are significantly deeper and wider. The metal film in some places is lifted from the GaN surface, and in other places, the surface of GaN is exposed. It appears that the surface of GaN, between the dislocations, was not degraded and remained flat (see arrows in Figure 3).

This phenomenon, the elevated temperature chemical instability of GaN defects exposed to either metal films or free surfaces, is very general in nature and has importance for GaN-based device design. Bulk GaN has the following decomposition reaction above 800°C: GaN $\rightarrow$ Ga(l)+N_2(g). Nevertheless, GaN films can survive higher temperatures due to the high stability of the (0001) surface. In addition, the reaction is sluggish due to kinetic difficulties recombining nitrogen atoms into N_2 molecules on the GaN surface. At locations where a dislocation exits GaN, the atomic arrangement is of lower stability and therefore triggers the decomposition of GaN (Figure 4). Nitrogen atoms may diffuse into the metal, recombine into molecules and form N_2 gas. Such gas accumulates under the metal film and exerts enough pressure to cause metal film de-cohesion (see Figure 3).

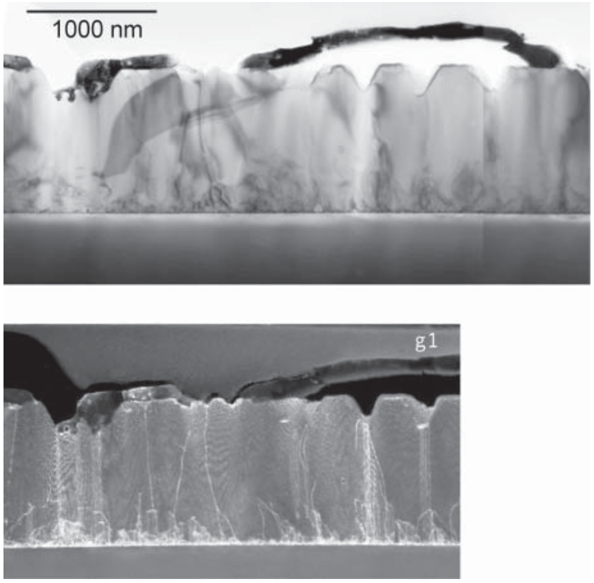


Figure 3: *Bright field (upper) and weak-beam dark field (bottom) images of the 800°C-annealed specimen.*

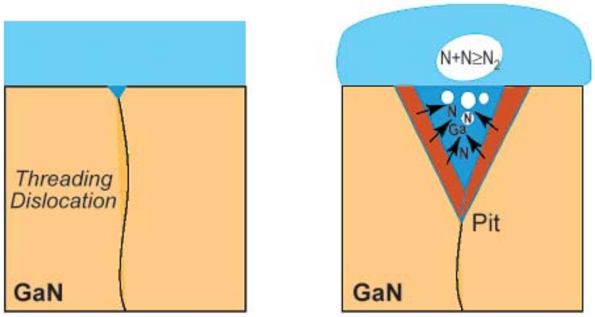


Figure 4: *Schematic drawing illustrating decomposition of GaN along a dislocation line and resulting in the formation of N_2.*

For More Information on this Topic

L.A. Bendersky, A.V. Davydov, W.J. Boettinger

Responding to the Auto Industry's Research Needs in Materials: Forming of Lightweight Materials

In response to a recommendation by the NIST Visiting Committee on Advanced Technology, the Industrial Liaison Office (ILO) was established to address the desire of NIST Senior Management for NIST to "close the loop with industry." In particular, although NIST receives excellent recognition for its work from industrial project leaders and bench level scientists and engineers, at higher levels of industrial R&D management, the impact of NIST's work is frequently unknown. Since the automotive industry, one of NIST's largest "customers," was chosen as a targeted sector, several projects within the MSEL Program on Forming of Lightweight Materials for Automotive Applications were selected to test the industry feedback process and answer the question: "Are we meeting industry's needs?" The feedback results were overwhelmingly positive.

The NIST Industrial Liaison Office (ILO) chose three projects within the Metallurgy Division to assess the impact of NIST Laboratory Programs on the auto industry:

- Standard Test Method Development for Sheet Metal Forming
- Microstructural Origins of Surface Roughening and Strain Localization
- Process Models for Metal–Matrix Composites

Detailed descriptions of the first two projects are contained in this annual report. The project on Process Models for MMCs was completed last year and was described in the FY01 annual report.

The ILO process began with the development of surveys that were targeted for a cross-section of researchers, managers, and directors in the automotive and associated industries. The surveys contained brief descriptions of the projects and provided web sites with more detailed project results. At this point, the respondents were queried as to their familiarity with the projects and whether the intended outputs were useful to their companies. A series of questions was designed to assess the impact of the projects on the automotive industry. Finally, the survey sought feedback as to whether some modifications to the projects or any other research would be more valuable than the current projects.

A list of potential industrial contacts was made for each project consisting of researchers, managers, and executive level staff from the appropriate companies. The ILO manager then contacted these individuals and requested their participation in the survey. The surveys were sent out only to those who agreed in advance to provide feedback to NIST. The ILO manager again contacted each individual to go over the survey. For the three projects mentioned, more than 50 surveys and interviews were completed.

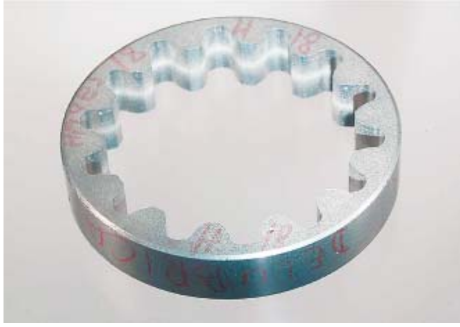


Figure 1: *A transmission fluid pump component showing centerline porosity (light band) predicted using process modeling shown in Figure 2.*

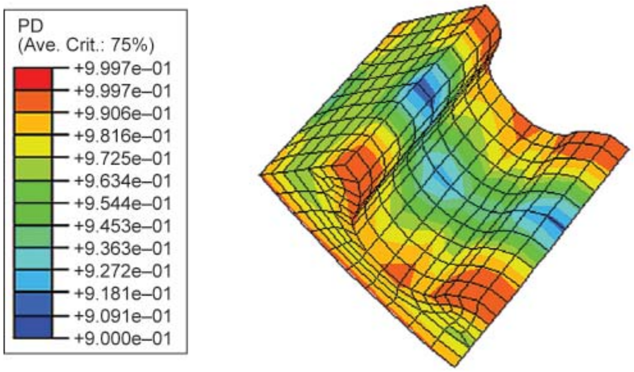


Figure 2: *Predicted density of the powder part which is shown in Figure 1. Note low density regions in the middle.*

Results of Surveys

Standard Test Method Development for Sheet Metal Forming

Objective: Enable the production of more accurate dies for auto body parts.

Approach: Produce, measure, and analyze multi-axially strained sheet samples.

Product: New standard tests and metrology to accurately determine sheet metal mechanical response under forming conditions.

Relevance: Enables use of lighter, high strength materials required to meet fuel efficiency goals.

Industry Response: The survey revealed that this project is already known and appreciated by a significant portion of the appropriate people in the auto industry. Its uniformly high scores for impact, value of output, and importance indicate that it would be mutually beneficial to extend this awareness to an even greater portion of the industry. The reviewers provided a list of potential new contacts. The addition of these new contacts to future communications by NIST researchers with the automotive industry will help expand the visibility of this project.

Impact of Survey on NIST: Following these surveys, the results were reviewed with the NIST researchers, the Group Leader, the Metallurgy Division Chief, and the MSEL Director. As a result of the survey, the NIST research team has been able to: (1) validate their priorities for materials to be tested, (2) reinforce the current priorities, (3) identify 13 new contacts, (4) learn of the desired form of communicating project results, (5) learn more about types of standard testing that already exist in industry, and (6) identify important future directions.

Figure 3: *A pre-standard cup test specimen used at NIST to measure formability and constitutive behavior under equibiaxial strain conditions.*

Microstructural Origins of Surface Roughening and Strain Localization

Objective: Develop measurement methods, models, and data that enable industry to predict the behavior of sheet metal in dies.

Approach: Explore the origins of inhomogeneous deformation and its quantification and behavior prediction for use in finite element codes.

Product: Microstructural and formability databases for aluminum and steel.

Relevance: By better understanding the interplay of the material and the stress states encountered within the die, the die tryout period can be reduced and significant cost savings realized.

Industry Response: The response was extremely positive. About 2/3 of the respondents were already aware of the project. Those who were not previously aware of this work became interested as they learned about it. The expected outputs were all considered to be useful and valuable. The window of opportunity was thought to be 12 months. Respondents felt the work was important and that NIST's assessment of its impact was valid. Only minor modifications were suggested. In particular, high-strength steel and advanced high-strength steel were mentioned as additional alloys of industrial interest. They are eager to establish communications with NIST to follow the progress of this project. The respondents supplied a number of new contacts.

Impact of Survey on NIST: The NIST research team will include several new steel alloys in the project. They also intend to communicate their results directly to the 13 new contacts identified during this process.

Process Models for Metal–Matrix Composites

Objective: Provide process models for the USAMP project "Low Cost Powder Metallurgy Technology for Particle Reinforced Aluminum (PRA)" to accelerate the introduction of PRA into auto parts and to capture the knowledge generated by the USAMP project in a readily usable form.

Approach: Provide models for lightweight metal consolidation, measurements and data for model validation, software that readily transfers the models, and data required to implement the models.

Product: Models and input data for commercial software.

Relevance: Enables use of lighter, high-strength materials required to meet fuel efficiency goals.

Industry Response: A limited number of responses were received, perhaps due to the fact that this project was already completed. "Expected outputs" were rated 4.3 out of 5, indicating high value. Three-quarters of the respondents agreed with NIST's assessment of the project's impacts and importance. Additional impacts were identified by the respondents. No modifications were suggested, but suggestions for future related projects with details were made.

Impact of Survey on NIST: An interesting issue was raised by the survey. A respondent who knew and approved of NIST's work did not understand that the modeling software developed by NIST and its partners is broadly applicable to powder consolidation of a wide range of alloys and conditions, not just those of direct interest to the USAMP project. Scientists sometimes assume that the generality of their work is understood; this is a communication issue that must be addressed in order to ensure the greatest impact and application of technical developments.

For More Information on this Topic

Standard Test Method Development for Sheet Metal Forming and Microstructural Origins of Surface Roughening and Strain Localization: T. Foecke, S. Banovic; *Process Models for Metal Matrix Composites:* R. Fields; *NIST Industrial Liaison Office and the impact of these projects on industry:* C. Allocca

Thermodynamic Database for Multicomponent Alloys

Commercial alloys rarely consist of only two elements and some contain up to 10 elements. Thermodynamic modeling allows the prediction of phase equilibria in multicomponent alloys from the extrapolation of the thermodynamic descriptions of the constituent binary and ternary systems. Different properties of a system, such as phase boundaries and enthalpies are described with one set of functions resulting in a consistent description of phase properties. The approach gives reasonable predictions for complex alloys, thereby providing a powerful tool for alloy design, and provides a compact storage method for large amounts of phase diagram and other thermodynamic data.

During the last decade, researchers from the Metallurgy Division have collaborated with scientists from universities and industry on several projects with emphasis on modeling tools for the design and manufacture of multicomponent alloys. The traditional approach for development of a new alloy relies on the knowledge and experience of the engineer, which can be costly due to the significant amount of testing required to obtain the correct properties.

Structural parts made from Ni-base superalloys not only must withstand extended periods of service at high temperatures, but also must tolerate severe environmental conditions, such as the highly corrosive environment of a jet engine. Higher operating temperatures result in increased performance demands for both aerospace applications, as well as land-based energy applications.

For a number of projects, including the NIST-sponsored Consortium on Casting of Aerospace Alloys, the DARPA sponsored Investment Casting Cooperative Arrangement, and the General Electric-lead DARPA project for Accelerated Insertion of Metallic Structural Materials (AIM), the Metallurgy Division has constructed a thermodynamic database for Ni-base alloys. The NIST Ni-superalloy thermodynamic database includes 10 elements, Ni-Al-Co-Cr-Hf-Mo-Re-Ta-Ti-W, and is based on critically-evaluated literature and NIST work. Phase equilibria can be calculated from this database. Since the immediate goal for the application of this database was for the modeling of single crystal alloys, the final refinement of the description in the database was restricted to the liquid, fcc-γ and L12-γ' phases. Figure 1 shows the comparison of experimental liquidus, solidus and solvus temperatures and those predicted from the calculation for a series of commercial superalloys. Experimental and calculated phase boundary data for the γ-γ' two-phase region are compared in Figure 2.

As a result of this work, detailed solidification behavior for Ni-base superalloys can be predicted. This improved the quality of solidification simulations for investment castings by providing more reliable predictions of casting defects allowing industry to eliminate the need for extensive testing of a series of castings to reach an acceptable design.

In addition to a dependence on the multicomponent thermodynamics, a wide variety of Ni-base superalloy applications are controlled by diffusion processes including solidification, homogenization, γ' precipitation, bonding and repairing processes, and protective bond coats. Many of these industrial problems can be addressed using a diffusion simulation code that combines composition-dependent diffusivities with multicomponent thermodynamics. The thermodynamic database was used for the development of a diffusion mobility database for Ni-base superalloys. The NIST mobility database can be used in conjunction with the NIST Ni-superalloy thermodynamic database, as well as with other commercial thermodynamic databases.

Electronic versions of the NIST databases have been distributed to various industries, universities, and national laboratories.

Most databases that are currently available to scientists, engineers and students need to be expanded and improved. A workshop on "Databases for Computational Thermodynamics and Diffusion Modeling" was held at NIST Gaithersburg, March 21–22, 2001. The workshop format was a series of invited talks given to the group as a whole followed by general discussions of needs and benefits. The workshop was attended by 39 registered participants of which 16 were from industry. Of the 17 oral presentations given, 8 were from industry,

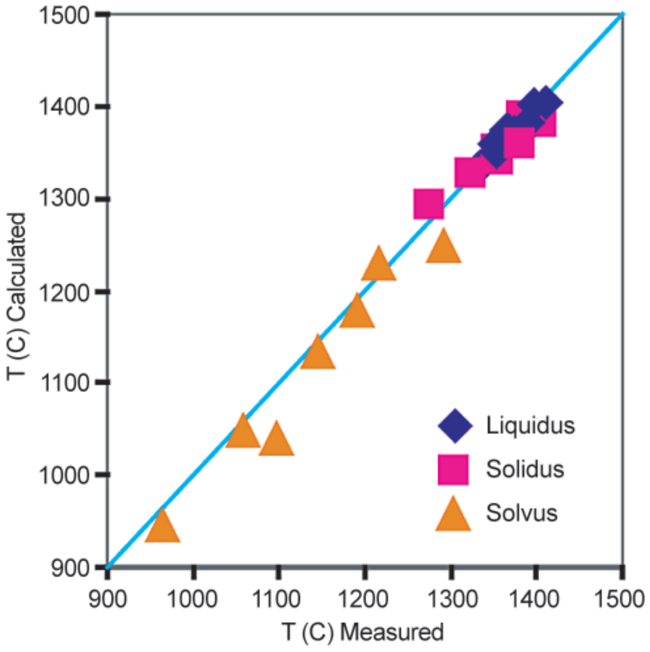


Figure 1: *Comparison of experimental and calculated liquidus, solidus and solvus temperatures of superalloys.*

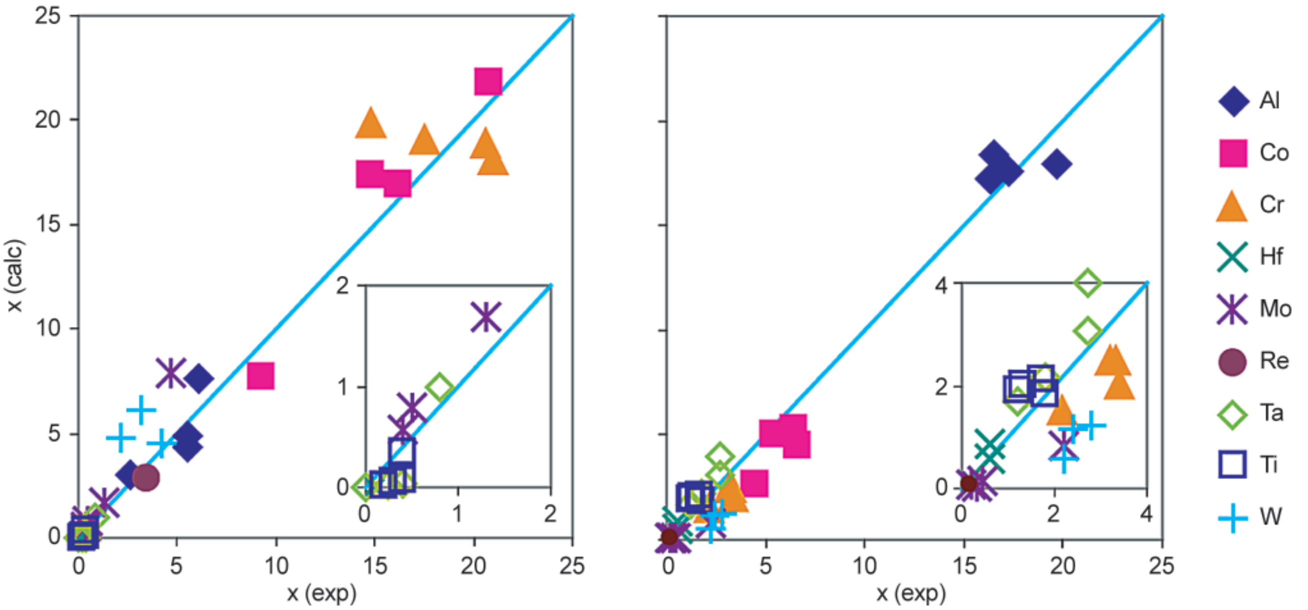


Figure 2: *Comparison of experimental and calculated phase boundary data for the γ-γ´ two phase region.*

emphasizing the applicability of the modeling approach to industrial processes. Extensive discussions followed the presentations.

The participants at the workshop agreed that, by the year 2010, it is highly likely that all Materials Science and Engineering students will learn to solve real world materials problems using modeling and simulation tools. The national benefits of providing materials engineers with software and databases for modeling materials and processing are savings in costs, energy and natural resources via optimization studies, as well as improved materials properties and development times. The primary deliverables of the workshop were, first, to identify the database and information delivery tool needs of industry and, second, to propose a roadmap for how these needs can be met.

Expanded collaborative efforts are needed in areas of materials education, basic research, and database development within the next decade to meet these needs. Working groups will be formed for each of these areas in FY2003. The primary objective for materials education identified at the workshop is to interest faculty and students in applied thermodynamics and kinetics by preparing a collection of applied problems. The current NSF program at Penn State University on computational thermodynamics and kinetics will serve as a model for improving abilities of students in these research areas. Basic research was identified to be of crucial importance to generate experimental, as well as calculated data from first-principles calculations. This requires a broad initiative to rebuild the thermodynamic and kinetic measurement infrastructure and to encourage theoretical *a priori* studies. The action items identified for public databases include encouragement of journal policies to require publication of parameters in assessment papers, recommendation and publication of a data format designed for portability of the thermodynamic parameters and fostering industrial user groups to identify software needs.

The second major activity for FY2002 was developing a relationship with SGTE (Scientific Group Thermodata Europe), one of the leaders in the world effort to develop thermodynamic databases for inorganic and metallurgical systems and their applications to practical, industrial problems. SGTE was originally a consortium founded by European centers active in database development. Today membership in SGTE is no longer limited to European organization and the NIST is being welcomed into the now international group. The aims of SGTE are the critical assessment and compilation of self-consistent thermodynamic data for both pure substances and solutions of all types. SGTE has pioneered the development of multicomponent databases. This includes compilation of the Gibbs energies of the pure elements, published by SGTE in 1991, thermodynamic properties of stoichiometric inorganic compounds in 1999 to 2001 and the planned publication of databases for binary systems. The self-consistency of the SGTE databases has made the thermodynamic quantities and model descriptions de facto standards for the construction of databases for multicomponent systems. Joining SGTE will enable NIST to contribute to the discussion of future model choices and cooperate in the broader international effort to unify thermodynamic data.

For More Information on this Topic

U.R. Kattner, W.J. Boettinger, C.E. Campbell (NIST/MSEL)

U.R. Kattner, CALPHAD and Alloy Thermodynamics, eds. P.E.A. Turchi, A. Gonis, and R.D. Shull, “Construction of a Thermodynamic Database for Ni-base Superalloys: A Case Study.” *TMS*, pp. 147–164, 2002.

Advanced Manufacturing Methods

An increasingly competitive manufacturing environment drives the search for new materials and processing techniques to make them. In most cases, materials processing steps determine the microstructure and performance of the material while manufacturing costs determine price. Industry needs measurement methods, standards, and data that will help monitor, control, and improve processing methods. These tools are also needed to help understand materials processing and to develop new processing methods and materials with enhanced properties. This is as true for highly developed, well-established industries as it is for rapidly growing or emerging industries. It is also true for all types of materials, processes, and products. The industrial competitiveness of the United States depends on U.S. manufacturers' ability to use the measurement tools to develop and advance their manufacturing methods. In many cases, the needed tools are generic and their impact would be greatly enhanced if they became industry wide standards. Therefore, MSEL is working to develop measurement methods and standards to enable industry to achieve these goals. This work is often being conducted in close collaboration with industry through consortia and standards organizations. The close working relationship developed with industry through these organizations not only ensures the relevance of the research projects, but also promotes an efficient and timely transfer of research information to industry for implementation. Since different materials and industries frequently have similar measurements needs, and most industrial products have multiple materials components, this program covers the processing of ceramics, metals, and polymers.

Research in the Ceramics Division focuses on development of test methods for the assessment of contact damage and wear, development of test methods and predictive models for evaluation of mechanical properties at elevated temperatures, and development of models for prediction of coating properties and performance. One project focuses on low temperature co-fired ceramics (LTCC), a manufacturing method being developed largely for portable wireless modules because it promises to allow for a reduction in the size and cost of modules used in high-frequency applications while improving performance. Because dimensional tolerances are critical in this process, accurate measurements and predictive models of dimensional changes during sintering are necessary for the commercialization of LTCC modules. Measurement methods and predictive models for the overall shrinkage and the local variations in sintering near vias and interconnects are being developed.

Projects in the Metallurgy Division cover several processing and measurement methods. The performance of metallic components in products is strongly dependent on processing conditions that determine microstructural features, such as grain size and shape, texture, the distribution of crystalline phases, macro- and microsegregation, and defect structure and distribution. Expertise is applied from a wide range of disciplines, including thermodynamics, electrochemistry, fluid mechanics, diffusion, x-ray, and thermal analysis, to develop measurement methods and understand the influence of processing steps for industries as diverse as automotive, aerospace, coatings, and microelectronics. Rapidly growing and emerging industries such as biotechnology and nanotechnology are dependent upon the development of new advanced manufacturing methods that can produce metallic components with the desired characteristics and performance. Current projects focus on measurements and predictive models needed by industry to design improved processing methods, provide better process control, develop improved alloy and coating properties, and reduce costs. Important processing problems being addressed include melting and solidification of welds, solidification of single crystals, powder production and consolidation, and coating production by thermal spray and electrodeposition.

Polymeric materials have become ubiquitous in the modern economy because of their ease of processing. However, these materials can exhibit complex and sometimes catastrophic responses to the forces imposed during manufacturing, thereby limiting processing rates and the ability to predict ultimate properties. The focus of the Polymers Division is directed towards microscale processing, modeling of processing instabilities, and on-line process monitoring of polymeric materials. Our unique extrusion visualization facility combines in-line microscopy and light scattering for the study of polymer blends, extrusion instabilities, and the action of additives. Current applications focus on understanding and controlling the "sharkskin instability" in polymer extrusion and observation of the dielectric properties of polymer nanocomposites. Fluorescence techniques are developed to measure critical process parameters such as polymer temperature and orientation that were hitherto inaccessible. These measurements are carried out in close collaboration with interested industrial partners.

Contact: Stephen D. Ridder

Modeling Solidification and Microstructure Evolution

Many properties of structural and functional materials depend on the distribution of composition, phases, grain orientations, and microstructure on the scale of 1–100 mm. Models of alloy eutectic solidification, dendrite coalescence and electrodeposition are being developed using several advanced computational methods. The goal of this research is to develop a suite of modeling tools for the evolution of complex microstructures for a wide variety of processes. These models are providing information to aid in designing materials processing systems that increase product yield and performance.

James A. Warren and William J. Boettinger

Modeling of the evolution of microstructure produced by solidification, electrodeposition and other processes involves mathematical solution of equations for heat flow, fluid flow, current flow and/or solute diffusion. Boundary conditions on external surfaces reflect the macroscopic processing conditions. Boundary conditions at internal interfaces correspond to the liquid-crystal (grain) or grain-grain interfaces. These internal interfaces are moving boundaries and require boundary conditions with thermodynamic and kinetic character. For solid-solid transformations, stress and strain replace fluid flow as a consideration.

In order to deal with the complex interfacial shapes that develop during solidification, electroplating and grain growth, the phase field method has become the technique of choice for computational materials scientists. This approach often requires numerical techniques to solve the model equations but readily deals with complex interface shapes and topology changes. The research, conducted in the Metallurgy Division, is supported in part by the NIST Center for Theoretical and Computational Materials Science.

Dendritic and eutectic growth is always present in castings and involves extremely complex interface shapes. Three major accomplishments of FY2002 deal with the application of diffuse interface modeling to these types of growth.

Classical treatments of eutectic characterization and morphology selection require *a priori* knowledge of the eutectic microstructure. The phase-field method does not suffer from this limitation and serves as a useful tool for predicting microstructures of multi-component eutectics where complicated phase arrangements occur. In FY2002, a phase field model for solidification of binary eutectics was developed, was validated by classical models for eutectic morphology selection, and is now being used in regimes well outside the validity of those classical models (Figure 1).

Phase field models of grain growth, pioneered at NIST, have been adopted by several other research groups, now investigating nucleation, polymer solidification, spherulitic growth and fractal structures. (See, for example, L. Gránásy, T. Börzsönyi, and T. Pusztai, Phys. Rev. Lett. 88, 206105 (2002)). A comprehensive overview of the physics of these models has been submitted for publication.

Solidification of metallic alloys has been extensively studied (dendrite tip kinetics, microsegregation, coarsening of dendrite arms, etc.), but surprisingly little is known about the last stage of solidification when the primary phase regions impinge. Yet, the details of the final stages of solidification of multigrain and/or dendritic materials have significant impact on casting defects such as hot tearing. Hot-tearing is caused by a lack of tensile strength of castings due to the thin continuous liquid film that remains between dendrite arms up to very high volume fraction of solid. It is therefore important to know when dendrite arms bridge (or coalesce) to form a coherent solid that can sustain tensile stresses. The details of the process determine the temperature at which a coherent solid forms; i.e., a solid that can sustain tensile stresses without rupture. Using one dimensional (1D) interface tracking calculations, diffusion in the solid phase perpendicular to the interface (back-diffusion) is shown to be a critical factor in determining the temperature where liquid finally disappears during solidification. To study the interaction of interface curvature and diffusion in the liquid film parallel to the interface, a multi-phase field approach has been used. After validating the method with the 1D interface tracking results for pure substances and alloys, the phase field approach shows that the coalescence process originates in small necks and involve rapidly changing liquid–solid interface curvatures. (M. Rappaz, A. Jacot and W.J. Boettinger, Metall. and Matls. Transactions, in press.)

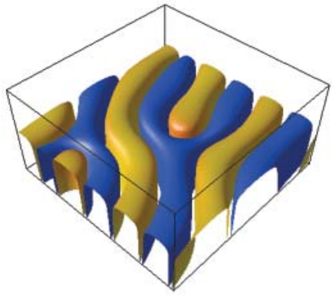


Figure 1: *A snapshot of the concentration field in the liquid, at the liquid–solid interface, of a three-dimensional phase field simulation of a directionally solidified binary eutectic alloy.*

Contributors and Collaborators

W. Boettinger, S. Coriell, J. Guyer, D. Lewis, R. Sekerka, G. McFadden (ITL); R. Kobayashi (Hokkaido University); W.C. Carter (MIT)

High Speed Machining

The U.S. spends $200 billion annually on machining of metal parts. Industry studies have shown that considerable improvements in the efficiency of these operations are possible. Also, the rapid development of tooling and high-speed machines makes traditional knowledge-based approaches to improved efficiency ineffective. Predictive modeling has been promoted by industry as a method to realize the improved efficiency. Through this project, NIST will provide measurement capabilities, materials data, and phase transformation models needed to make accurate predictions.

Richard J. Fields, William J. Boettinger, and Carelyn E. Campbell

Machining of metal parts, e.g. turning, milling, drilling, broaching, etc., to required dimensional tolerances is an essential part of many manufacturing processes. Efficient processes can greatly reduce the price of a part and enhance the competitive position of the manufacturer. A recent industry survey found that industry chooses the correct tool for machining a part less than 50% of the time. Advances in spindles and tooling stimulated by the NIST Advanced Technology Program (ATP) now requires that the traditional, experience-based approaches to finding the optimal process parameters such as feed rate, cutting rate, tool material, tool shape, etc., be replaced by modeling and simulation. While initial results are impressive, data are still needed to validate the models and run the simulations.

The current project is advancing the state-of-the-art in two complementary areas: 1) measurement of fundamental data on the behavior of materials at the extreme strain and heating rates needed for input into the models, and 2) modeling and characterization of the microstructural changes that occur during the severe deformation and heating in real machining operations. Measurements of residual stress, responsible for part distortion after machining, are also being conducted at the NIST Center for Neutron Research within MSEL.

The first research effort is directed at obtaining materials data, which has required an extension of our current capabilities in high-rate heating to include high rate straining. Three significant activities have been completed. First, a “high-heating-rate model” of the modified Hopkinson bar compression test device has been created, allowing us to explore various approaches to obtaining uniform heating of samples during testing. Second, a Hopkinson bar compression tester has been constructed that provides strain rates on the order of $10^{5}\ \text{s}^{-1}$ (Figure 1) and heating rates of $10^{3}\ \text{Ks}^{-1}$. Third, calibrations were completed that assure that the temperatures measured during the high rates of heating are accurate. The facility will be used to develop databases on a variety of materials of interest to the machining industry. These data will be used in simulations of prototypical machining operations and compared to the advanced machine metrological database. Evaluation of various models and simulations will provide direction to future research.

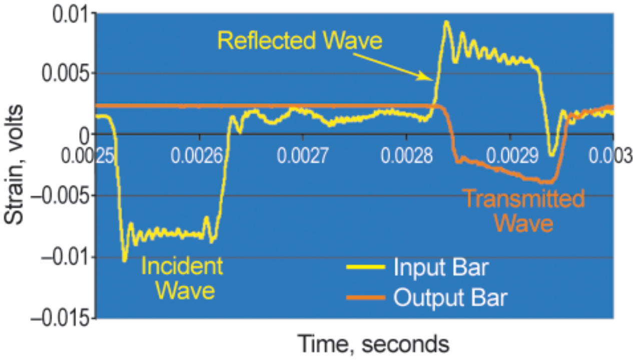


Figure 1: *Stress waves recorded on the input and output bars of the split Hopkinson bar. Reflected and transmitted waves provide data to calculate the dynamic stress–strain behavior.*

The second research effort focuses on characterizing and modeling microstructure changes in the deformation/hot zone of Al alloys during machining. Generally, significant softening occurs when precipitation hardened Al alloys are heated due to coarsening of the precipitate structure. Structure and dislocation density will be measured. A model that uses temperature vs time data from thermal images from the Physics Laboratory (Figure 2) will be used as input to a microstructure model. The model will employ thermodynamics and diffusion kinetics to predict microstructure changes.

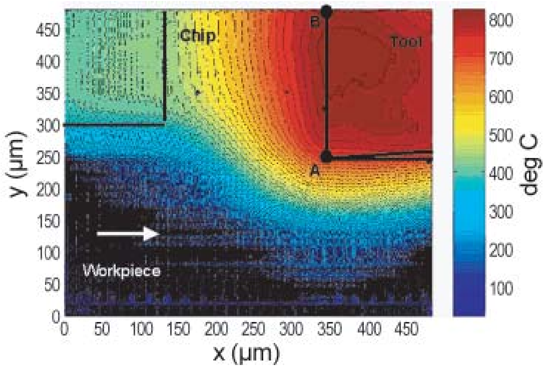


Figure 2: *Thermal profile of a steel tube undergoing orthogonal cutting.*

Contributors and Collaborators

D. Basak, L. Levine, R. deWit, H. Prask (NIST/MSEL); M. Davies, R. Rhorer, R. Polvani, K. Jurrens, B. Dutterer, M. Kennedy, R. Ivester, H. Soons (NIST/MEL); T. Burns (NIST/ITL); H. Yoon (NIST/PL)

Metal Powder Processing

As engineering design requirements for Powder Metal (PM) parts become more demanding, powder size requirements have progressively dropped in average size and narrowed in size distribution range. The NIST Metallurgy Division atomization facility has been a test-bed for providing the PM industry with material property data and processing procedures for improving yield of desirable powder size distributions. This information will be provided in a comprehensive "Gas Atomization Recommended Practice Guide" to be published following a PM industry review in December 2002.

Stephen D. Ridder

Gas atomization is the primary source of material for many advanced Powder Metal (PM) processing procedures such as Powder Injection Molding (PIM), Hot Isostatic Press (HIP) consolidation, and Thermal Spray (TS) coatings. These processes are used to produce surgical tools and appliances, aircraft and power turbine engine parts, severe service parts for the petrochemical industry, and increasing numbers of critical automotive components. Powder size, because of its affects on microstructure, powder handling, and consolidation, controls the resulting PM material properties. The cost to produce these optimum powder size distributions can become prohibitively expensive when using traditional gas atomization techniques that require screening of the powder product for usable powder and recycling the waste. Research collaborators representing the major gas atomization companies and national laboratories have participated in various projects aimed at sensor development, alloy chemistry, particle size control, and powder characterization. Currently available information to be included in a NIST SP (Special Publication), "Gas Atomization Recommended Practice Guide," includes: 1) sensors and control techniques to optimize the Gas to Metal mass flow-rate Ratio (GMR), 2) gas jet geometry designs that reduce adverse shock wave generation, and 3) advanced process control software that incorporates atomization plume video frames and "knowledge base" heuristics. This NIST SP will be available for discussion by PM industry participants at a workshop to be held at NIST in December 2002.

Results from current aerodynamic studies of the supersonic gas flow produced by the atomizing nozzle will be published as a supplement to the NIST SP. Experimental evidence from a variety of sources has suggested that axial length scales have an important role in determining particle size distributions. Finer particle sizes tend to be produced when the length of supersonic gas velocity is extended in the axial direction. An extended supersonic zone improves secondary droplet atomization far from the nozzle tip (Figure 1), ultimately leading to finer powder. Because axial length scales have often been overlooked in the design of atomizing nozzles, opportunities exist for improving performance. For example, by designing nozzles to produce a specific axial supersonic velocity profile to achieve a desired size distribution, off-target particle size yields might be reduced, improving efficiency and reducing powder costs.

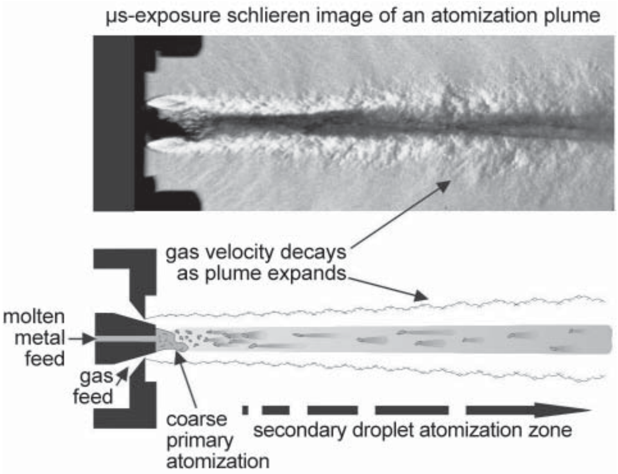


Figure 1: *Anatomy of a gas atomization plume.*

Before such benefits can be realized in practice, however, key questions must be addressed. Chief among these is determining the degree to which the supersonic length affects particle size. In practice, supersonic length is typically coupled with changes in gas velocity and dynamic pressure that also tend to refine particle size. Research efforts at NIST are therefore aimed at isolating the effect of supersonic length on particle size. Preliminary atomization experiments performed and presented to powder producers in FY2002 have shown that a 20% increase in supersonic length reduces median particle size by 10% [Ref. 1]. A soon-to-be installed vacuum system will expand the range of supersonic lengths that can be achieved and definitive experiments on supersonic gas flow will be completed in FY2003. Our goal is to have the results from this research incorporated into general design guidelines for gas atomizer nozzles.

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[1] S.P. Mates, F.S. Biancaniello and S.D. Ridder, "An Alternative View of Close-Coupled Gas Atomization of Liquid Metals," *PM^{2}TEC Proceedings*, MPIF, 2002.

Contributors and Collaborators

F.S. Biancaniello, R.D. Jiggetts, S.P. Mates

Electrochemical Processing of Nanoscale Materials

Precise temporal control of supersaturation provided by electrochemical methods holds promise for the synthesis and characterization of materials and structures of very small dimensions — nanomaterials. Variation of the electrochemical potential leads not only to changes in the metal deposition rate but also effects the adsorption of surfactants and segregation phenomena which exert a strong influence on the morphological evolution. Experiments are underway to explore the effect of manipulated growth schemes on roughness development during epitaxial film growth.

Thomas P. Moffat

Electrochemical synthesis has become an important tool in the fabrication of novel nanoscale devices and structures. Modulation of the electrode potential can be used to create films with a corresponding variation in composition and/or structure. This allows materials to be engineered with submonolayer precision. Looking to the future, exploitation of this technology will require a deeper understanding of potential dependent adsorption phenomena and its influence on morphological evolution during thin film growth. Several model systems are being examined at NIST which deal with issues important to both homo and heteroepitaxial film growth. A central aspect of this work is the combined use of atomic force and *in situ* scanning tunneling microscopy to probe the connection between atomistic processes and morphological evolution that occurs at larger length scales.

Halide adsorption on copper represents a model system for such study. At potentials corresponding to the copper/cupric ion equilibrium, the surface is saturated with an ordered 2-D chloride adlayer which in the case of Cu(100) results in step faceting in the <100> direction. The adlayer floats on the surface during deposition and at low overpotentials pyramidal growth is observed with the in-plane orientation determined by the halide overlayer. At more negative potentials a transition from pyramidal to block-like growth is observed. The correlation between the 3-D growth transition and the known potential driven 2-D order–disorder phase transition in the halide adlayer is being examined. By varying the metal cation and halide electrolyte concentration, the relative contribution of the potential dependence of the metal deposition rate versus the dynamics of surface transport are being investigated. In the limit where metal deposition rate is under transport control, the effect of potential modulation on electrocrystallization events may be studied independent of its effect on the metal deposition kinetics. Related work is underway using underpotential deposition of simple metals, such as Pb, to be used in place of, or in combination with, anions. In this instance, the role of a coverage dependent alloying–dealloying transition is being examined with an eye towards understanding both surfactant and solute trapping effects. These processes are important in the production of alloy for applications ranging from microelectronics to fuel cell catalysts to biosensors.

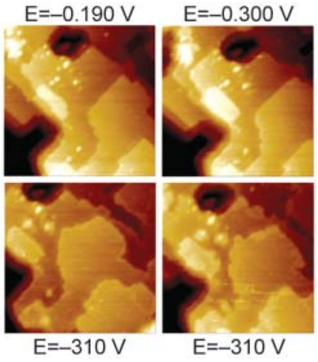


Figure 1: *A time sequence (right to left) of in-situ (70 nmx 70 nm) STM images of Pb deposition (bright contrast) at step edges on a chloride covered Cu(100) surface.*

In addition to our electroanalytical studies, pulse potential deposition is also being used to synthesize strained-layer superlattices of Co/Cu on semiconductors. In particular, ferromagnetic/semiconductor junctions are of interest for spin injection and detection in semiconductors. Interface structure is thought to play a critical role in the efficiency of spin transmission although limited experimental data exist. In the past year, we have examined the structure and magnetic properties of electrodeposited Co films on (001) n-GaAs. The films exhibit a strong hcp Co(1120)[001]||GaAs(001)[110] texture which is mediated by a thin interfacial bcc-Co phase.

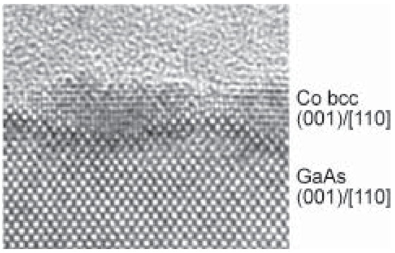


Figure 2: *A thin metastable bcc Co film electrodeposited on GaAs with a cube-on-cube epitaxial orientation.*

The results of this project have led to a new project in FY2003 to be focused on using in-situ STM techniques for characterizing the surface reactivity of immersed interfaces relevant to biological and electronic device design.

Contributors and Collaborators

J.E. Bonevich, R.D. McMichael, M. Vaudin, A. Ford (NIST/SURF); J. Mallett, W. Schwarzacher (Fulbright Scholar from University of Bristol)

Instrumented Consolidation of Amorphous Powders

Recent developments in production of amorphous materials have resulted in a class of iron- and aluminum-based powders that exhibit plastic behavior in the absence of dislocations. Potential applications for these materials have motivated industrial interest in consolidating the powders into parts. The Metallurgy Division is using instrumented consolidation with warm gas and liquid phase pressurizing media to understand the kinetics of densification of noncrystalline materials, avoiding the deleterious effects of hot pressing or sintering that would cause crystallization.

Stephen D. Ridder and Richard J. Fields

Amorphous metallic alloys have been known for many years, but they have been mainly an academic curiosity. Attempts have been made to use them industrially, but most of these have met with failure. Recently, Boeing has identified a class of amorphous materials based on aluminum which may be used in airframes. This class of materials also includes an iron-based alloy. Some of these alloys can only be produced as powders. To use them, it is necessary to consolidate them without crystallization or with carefully controlled fine crystallization. An interesting feature of these amorphous alloys is that they can be deformed plastically despite the absence of dislocations. The phenomenon behind this behavior is unknown, although the hypothesis of Spaepen and Turnbull {Scripta Met. 8, 563 (1975)} seems applicable. In any case, the ability to deform plastically suggests that pressure would be effective in consolidation. We have shown that to be the case (Figure 1). To understand the densification behavior of these materials, a project was initiated to study the kinetics of consolidation by pressure and heat below the crystallization temperature.

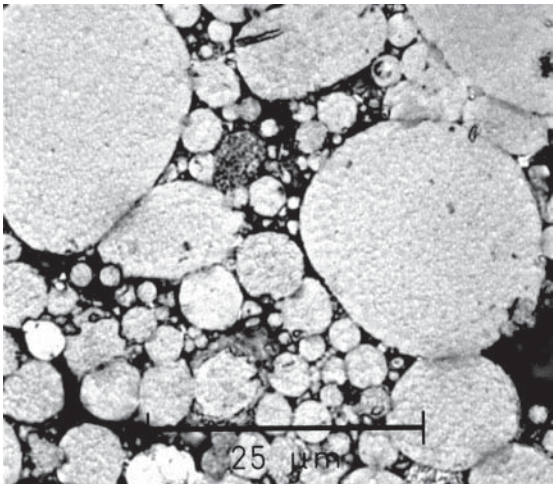


Figure 1: *Micrograph of pressed amorphous aluminum alloy showing plastic yielding of powder particle contacts. This compact attained a relative density of about 80%.*

Several approaches are being pursued. The hot isostatic press (HIP) has been instrumented with the sensor developed at NIST to follow densification (Figure 2). The warm isostatic press that uses a liquid ester and can be pressurized to twice the pressure of the HIP is also being instrumented with another density sensor developed at NIST. These two units provide quantitative, real time monitoring of the progress of densification (Figure 3). Relative densities of more than 86% have been obtained using these methods.

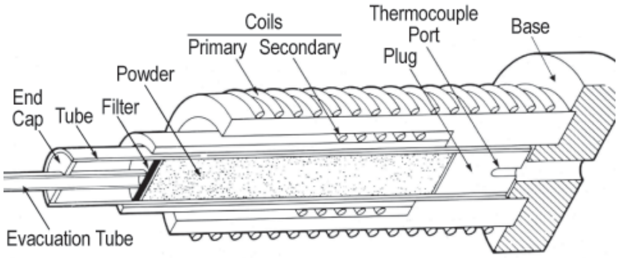


Figure 2: *Schematic diagram of NIST's eddy-current based density sensor for* in-situ *monitoring of hot isostatic pressing.*

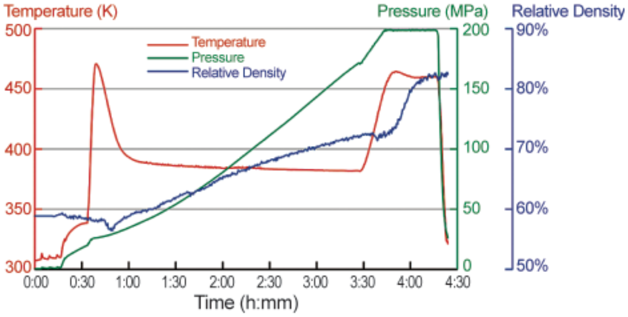


Figure 3: *The instrumented HIP provides continuous information about the applied temperature, pressure, and resultant density of the sample as shown by this record.*

It is also intended to investigate the use of dynamic consolidation, and electric field and current assisted consolidation to break down the oxide that is usually present on these powders. This surface oxide is a great hindrance to effective consolidation. The Kolsky Bar Facility, discussed in the project report on High Speed Machining, will be used for this effort.

Contributors and Collaborators

F. Biancaniello, R. Jiggetts, T. Pierce, T. Zahrah (MatSys); R. Rowland (MatSys); M. Blackburn (University of Connecticut); D. Bowden (Boeing); L. Christodoulou (DARPA)

Combinatorial Methods

The Combinatorial Methods Program develops novel high-throughput measurement techniques and combinatorial experimental strategies specifically geared towards materials research. These tools enable the industrial and research communities to rapidly acquire and analyze physical and chemical data, thereby accelerating the pace of materials discovery and knowledge generation. By providing measurement infrastructure, standards, and protocols, and expanding existing capabilities relevant to combinatorial approaches, the Combinatorial Methods Program lowers barriers to the widespread industrial implementation of this new R&D paradigm.

The Combinatorial Methods Program has adopted a two-pronged strategy for meeting these goals. The first of these is an active research and development program designed to better tailor combinatorial methods for the materials sciences and extend the state of the art in combinatorial techniques. Measurement tools and techniques are developed to prepare and characterize combinatorial materials libraries, often by utilizing miniaturization, parallel experimentation, and a high degree of automation. A key concern in this effort is the validation of these new approaches with respect to traditional "one at a time" experimental strategies. Accordingly, demonstrations of the applicability of combinatorial methods to materials research problems provide the scientific credibility needed to engender wider acceptance of these techniques in the industrial and academic sectors. In addition, the successful adoption of the combinatorial approach involves a highly developed "workflow" scheme. All aspects of combinatorial research, from sample "library" design and library preparation to high-throughput assay and analysis, must be integrated through an informatics framework which enables iterative refinement of measurements and experimental aims. Combinatorial Methods Program research projects give illustrations of how these processes are implemented effectively in a research setting.

NIST-wide research collaborations, facilitated by the Combinatorial Methods Program, have produced a wide range of new proficiencies in combinatorial techniques which are detailed in a brochure, "Combinatorial Methods at NIST" (NISTIR 6730), and online at *www.nist.gov/combi*. Within MSEL, novel methods for combinatorial library preparation are designed to encompass variations of diverse physical and chemical properties, such as composition, film thickness, processing temperature, surface energy, chemical functionality, UV-exposure, and topographic patterning of organic and inorganic materials ranging from polymers to nanocomposites to ceramics. In addition, new instrumentation and techniques enable the high-throughput measurements of adhesion, mechanical properties, and failure mechanisms, among others. The combinatorial effort extends to multiphase, electronic, and magnetic materials, including biomaterials assays. On-line data analysis tools, process control methodology, and data archival methods are also being developed as part of the Program's informatics effort.

The second aspect of the Combinatorial Methods Program is an outreach effort designed to facilitate technology transfer with institutions interested in acquiring combinatorial capabilities. The centerpiece of this effort is the NIST Combinatorial Methods Center (NCMC), an industry-university-government consortium organized by MSEL that became operational on January 23, 2002 via a kick-off meeting in San Diego. Although it is still in the growth stage, the impact of NCMC activities is readily apparent as 11 industrial partners and the Air Force Research Lab have already joined the NCMC membership program. The NCMC facilitates direct interaction between NIST staff and these industrial partners, and provides a conduit by which Combinatorial Methods Program research products, best practices and protocols, instrument schematics and specifications, and other combinatorial-related information can be effectively disseminated. This outreach is mediated in large part by a series of tri-annual workshops for NCMC members. The first NCMC meeting, "Library Design and Calibration," was held on April 26, 2002 at NIST, and it provided information essential to starting a combinatorial research effort. The second meeting (October 2002) will concentrate on combinatorial approaches to adhesion and mechanical properties. Further information on NCMC can be found on the website at *www.nist.gov/combi*.

Contact: Leonid A. Bendersky

Combinatorial Materials Research: Interconnects to Optoelectronic Materials

GaN and related nitrides have been identified as important materials for the realization of solid-state lighting, UV/blue lasers, LEDs and photodetectors. The engineering of improved electrical contacts to these devices is of particular industrial importance. This project develops a strategy for industry to reduce contact resistance, increase visible light transmittance, and improve thermal and mechanical stability of ohmic contacts to a variety of optoelectronic devices. Due to the large number of possible materials combinations and process variables involved, a combinatorial approach is valuable.

Albert V. Davydov and Leonid A. Bendersky

Typical electrical contacts to p-type GaN devices consist of thin film Au/Ni bi-layers, but contact resistance and reliability are far from ideal. The goal of this project is to establish techniques for industry to use to rapidly develop improved contacts for GaN and other compound semiconductor devices. A combinatorial approach (looking at Au/Ni ratio and metal film thickness) integrated with thermodynamic and diffusion modeling is being used to quantify the relationship between physical properties such as electrical resistance and optical transmittance of metal contacts and the fundamental microstructural and compositional properties of the metal-to-GaN interface.

Thermodynamic information and diffusion data are being evaluated for the Au-Ni-Ga-N system to help interpret the metallurgical reactions in the Au/Ni/GaN structures. To date, we have measured the thermal stability of the GaN compound and modeled the P-T-composition phase diagram for the Ga-N system. In addition, the Ni-Ga-N phase diagram has been evaluated experimentally and thermodynamically and presented at the CALPHAD-2002 Meeting.

A combinatorial array of Ni/Au bi-layer contacts of varying compositions has been fabricated by physical vapor deposition (e-beam evaporation) on commercial GaN wafers. The thickness of each metal layer varied discretely from 5 to 85 nm using a motion-controlled shutter system, producing an array of 88 elements (Figure 1(a)). The composition and microstructure of the contacts were examined with XRD (with Prof. I. Takeuch, UMD), optical microscopy, SEM and AFM. The transparency of metal layers to visible light was determined by reflectometry and transmission measurements. From transmission and XRD measurements (Figure 1b, c), we have identified library elements with optimum as-deposited Au/Ni compositions that are highly transparent and of good crystalline quality with epitaxial metal layers.

In FY2003, we will fabricate combinatorial libraries with an extended compositional range to develop thermodynamic stability data for GaN with other metal contact materials as well as continue to establish the analysis techniques for quantifying phase transformations and interdiffusion in these GaN/metal contact systems and developing the relationships between phase transformations, microstructures, and electrical performance.

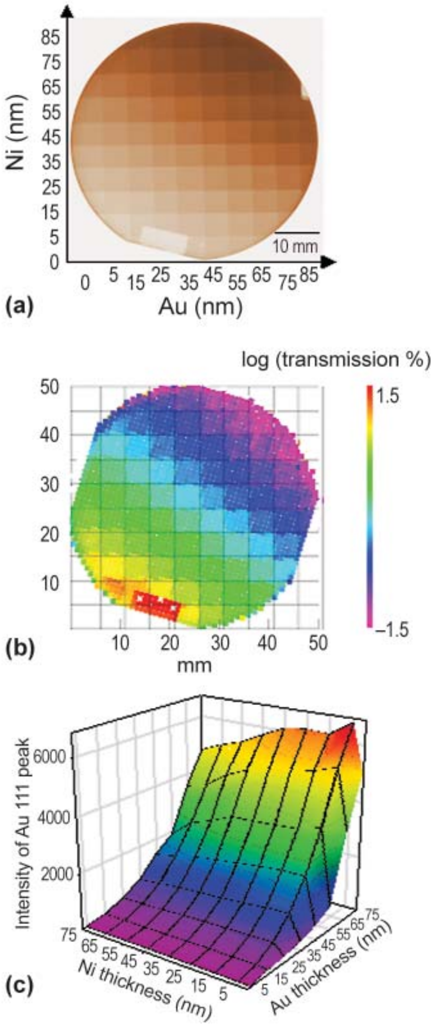


Figure 1: *(a) Array of as-deposited Au/Ni bi-layered metallization (88 elements) on 2-inch GaN/sapphire wafer; (b) Optical transmission imaging of the above sample at l = 450 – 713 nm; (c) XRD mapping of Au 111 reflection from all 88 Au/Ni elements.*

Contributors and Collaborators

W.J. Boettinger, D. Josell, A.J. Shapiro (Metallurgy Division, MSEL); P.K. Schenck, J.E. Blendell (Ceramic Division, MSEL); I. Takeuchi (University of Maryland); V.A. Dmitriev (Technologies and Devices International, Inc.)

Combinatorial Methods for Thin Films

In the search for materials for use in high-performance communication technologies, complex oxide phases with various chemistry and structural states are under consideration. With the relatively new ability to measure dielectric and magnetic properties locally, combinatorial methods can be used to create miniature thin film assays designed to either search for compositions with an optimal set of physical properties or study fundamentals of the relationship between crystallo-chemistry and physical properties, e.g., electric polarization or magnetic ordering in complex oxides.

Leonid A. Bendersky

The effectiveness of the combinatorial approach to thin film electronic materials has recently been demonstrated. In this approach, in order to rapidly survey a large compositional landscape, combinatorial assays with continuously changing compositions are synthesized, processed, and measured in a single experiment. Dielectric, magnetic and other physical properties of the compositional spreads can be measured by using recently developed instruments with high spatial resolution, such as microwave microscopes and microSQUIDs.

This project involves a close collaboration with the laboratory of Dr. I. Takeuchi (University of Maryland) where the combinatorial assays of oxide thin films are prepared by shutter-controlled pulsed laser ablation. NIST efforts are focused on detailed structural characterization of critical samples using transmission electron microscopy (TEM). Such characterization provides knowledge essential for understanding the deposition process and the correlations between physical properties and local microstructures.

We have investigated $BaTiO_3$-$SrTiO_3$ spreads in order to find correlations between microstructural defects and measured local dielectric properties. These materials have important properties suitable for tunable microwave devices. In our work, we identified the presence of a high density of planar defects in thin film layers adjacent to the substrates. Careful high-resolution TEM and electron energy loss spectroscopy (EELS) mapping and simulation of contrast established that the defects belong to $1/2<110>$ non-conservative stacking faults with a double layer of TiO_6 octahedra. Such defects result from the specifics of island growth, substrate/film mismatch and deviations from the Ba/Ti = 1 stoichiometry.

The ZnO-MgO system also exhibits a compositional spread in thin film form where a tunable bandgap is obtained by doping the semiconductor ZnO (bandgap 3.3 eV) with MgO (bandgap 7.8 eV). Potential applications are in optical devices, including UV lasers, as well as transparent conducting layers for solar cells and phosphors. Epitaxial spreads were comprehensively studied for UV transmission and for microstructure by scanning microdiffractometer and TEM. The results show a continuously changing bandgap thereby allowing the material to be considered for an array of photodetectors with a range of detection frequencies separately active at different locations on the patterned film.

In another facet of this project, a new method of rapid determination of ferromagnetic phase boundaries has been developed and used to examine composition gradients in thin films of $LaMnO_3$-$CaMnO_3$, a material which has attracted a great deal of attention for a strong colossal magneto-resistance effect. A high-resolution magneto-optical imaging technique was used to image stray magnetic fields at the edge of ferro/ferrimagnetic phases, thus directly visualizing phase boundaries in a temperature-composition space (Figure 1). The first application of the method has demonstrated its efficiency and accuracy as a combinatorial screening tool.

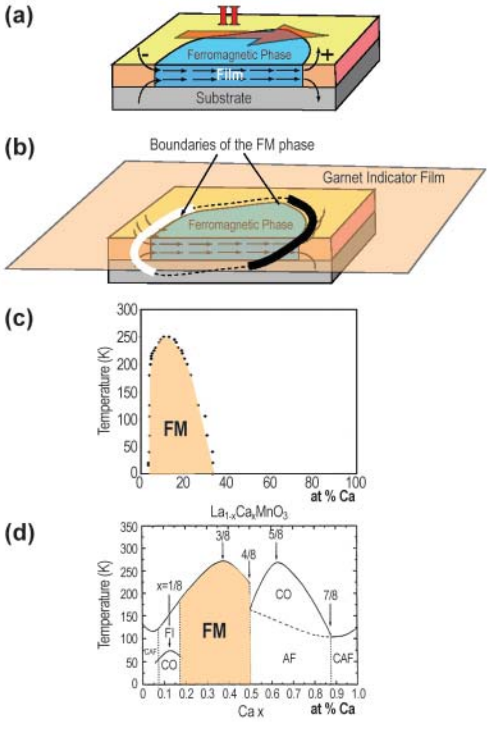


Figure 1: *(a, b) Schematic drawing showing the formation of a black/white pair of lines outlining boundaries of a ferromagnetic phase; (c) an experimental T-C diagram of a ferromagnetic phase in a thin film form; (d) diagram of the* $(La,Ca)MnO_3$ *system obtained for bulk ceramics.*

Contributors and Collaborators

L.A. Bendersky, C.J. Lu, R. Parke, M. Turchinskaya (MSEL); J.H. Scott (CSTL); I. Takeuchi, K.S. Chang (University of Maryland)

Data Evaluation and Delivery

Accurate materials data are increasingly critical to the rapid design and manufacture of the cost-effective, reliable products that characterize 21st century life. The MSEL Data Evaluation and Delivery Program is working to facilitate the building of interoperable materials structure, phase, and property databases needed by the scientific and industrial communities, and to develop strategies for visualizing multi-dimensional datasets needed for materials selection in product design.

To this end, the FY2002 Projects in the MSEL Data Evaluation and Delivery Program were focused on:

- Improving materials data transfer between databases through development of a standard materials mark-up language (MatML);
- Developing a major compilation of elastic moduli data for polycrystalline oxide ceramics;
- Providing protocols for data evaluation to ensure that databases are populated with accurate data;
- Expanding the Ceramics WebBook which provides links to other sources of ceramic data and manufacturer's information, as well as selected data sets evaluated by NIST, including structural ceramics and high temperature superconductor databases, glossaries, and tools for analysis of ceramic materials;
- Completing the first release of a new Windows-based PC product for the Inorganic Crystal Structure Database in cooperation with Fachinformationszentrum (FIZ) Germany
- Producing phase diagrams through the NIST/American Ceramic Society, Phase Equilibria Program;
- Developing approaches to viewing multidimensional mechanical property and phase diagram data for metals, through a series of simple — but useful — interactive calculations;
- Establishing a prototype site for linking NIST materials data with external datasets such as those developed and maintained by ASM International; and
- Developing a comprehensive database of critically evaluated properties of lead-free solders including multi-dimensional data from three national consortia, the National Center for Manufacturing Sciences (NCMS) Lead-Free Solder Project, the NCMS Fatigue Resistant Lead-Free Solder Project, and the National Electronics Manufacturing Initiative (NEMI) Lead-Free Assembly Project.

Contact: Carlos R. Beauchamp

Reaction Path Analysis in Multicomponent Systems

Many commercial processes rely on multicomponent diffusion to control the formation and dissolution of precipitate phases within the matrix phase or at an interface. Development of a diffusion mobility database provides an efficient method to store a wealth of diffusion data and enables the means to extrapolate the available data to higher-order systems. The developed Ni-based diffusion mobility database enables the modeling of a variety of processes, including non-isothermal precipitation of γ´, heat-treatment optimization, solidification, transient liquid phase bonding, and coating applications.

Carelyn E. Campbell and William J. Boettinger

Multicomponent diffusion is important in many industrial processes, especially in the processing and application of Ni-based superalloys. An *a priori* understanding of diffusion-controlled microstructures would allow the optimization of heat treatments that avoid incipient melting and the prediction of freezing temperatures and solidification paths for Ni-based superalloys. All of these processes require the use of a diffusion mobility database to describe the composition-dependent diffusion coefficients.

Diffusion Mobility Database

Concentration-dependent diffusion coefficients in a multicomponent system are defined as the product of a thermodynamic factor and a mobility term. The NIST composition-dependent mobility database is constructed using an approach, which assumes that quaternary and higher order interactions are negligible. Thus, binary and ternary effects can be combined to extrapolate to higher order systems. For the Ni-Al-Cr-Co-Fe-Hf-Mo-Nb-Re-Ta-Ti-W system, a diffusion mobility database has been constructed for the γ (disordered FCC) phase. The current database includes only binary interactions. The development of this diffusion mobility database was published in *Acta Materialia* in 2002 where it is readily available to industry. General Electric Corporate Research and Development (GE-CRD) and Howmet Corporation provided results from multicomponent diffusion couples, which were compared with diffusion simulations. The experimental and calculated diffusion composition profiles for the Rene-N4/Rene-N5 diffusion couple agree quite well (Figure 1). The predicted location of maximum porosity also compared favorably to the observed pore formation. Figure 2 shows a back-scatter image of the 100 h sample and the location of the predicted porosity. Results from this couple and other multicomponent diffusion couples are evaluated and used to refine the current diffusion mobility database.

Applications

As a part of a General-Electric-led DARPA/AIM project, the γ´ precipitation process is being numerically modeled by, team member, Questek Innovations. This model requires inputs of equilibrium chemical potentials of γ and γ´, the composition dependent diffusivity in the γ matrix, γ and γ´ lattice parameters, and interfacial energy. NIST has provided Questek with an electronic version of the diffusion database to calculate the necessary diffusion coefficients. NIST has also initiated an effort to develop heat treatment optimization techniques to address industry's need for more efficient heat-treating practices of cast Ni-based superalloys. The ideal heat treatment of a cast Ni-base superalloy consists of a heating schedule that avoids incipient melting while minimizing either the power expenditure or the heating time to achieve a homogeneous single phase structure.

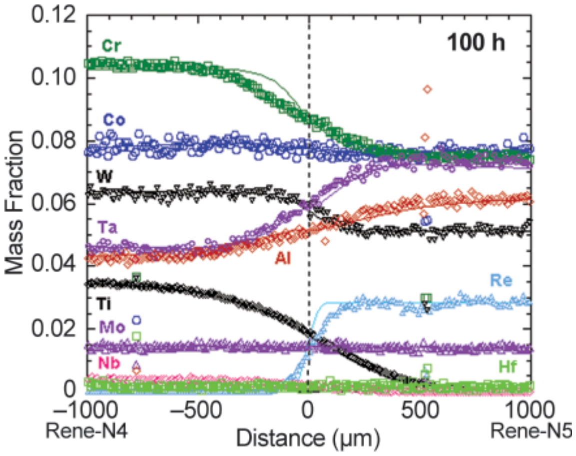


Figure 1: *Calculated (solid lines) and experimental (symbols) composition profiles for the Rene-N4/Rene-N5 diffusion couple at 1293°C for 100 h.*

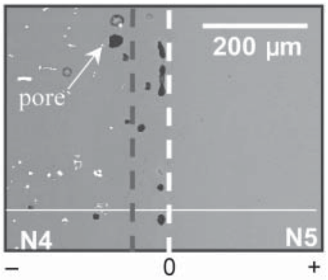


Figure 2: *Back scatter image of Rene-N4/Rene-N5 after 100 h at 1293°C. Thin white line indicates the position of microprobe scan. The dashed white line corresponds to the Matano interface. The dashed black line is the location of the predicted maximum porosity.*

Contributors and Collaborators

U.R. Kattner, B. Mueller, T. Hansen (Howmet Corp.); J.C. Zhao (GE-CRD); T. Helander (Thermo-Calc Software AB); C. Kuehmann, H. Jou (Questek Innovations); Z.K. Liu (Penn State); G. Ghosh, D. Seidman, P. Voorhees (Northwestern University)

Thermodynamic Databases for Industrial Processes

Many industries that process and use metals, from microelectronics to aerospace, need data for complex alloys (three or more components). The number of images that would be needed for graphical representation of these data is prohibitively large. Thus the development of thermodynamic databases that permit extrapolation of binary and ternary systems to higher order systems is needed. Access to these databases through an internet site with interactive software tools will allow the user to retrieve the needed phase diagram information.

Ursula R. Kattner

In order to deliver materials data efficiently to the end user, it is important to present technical data in a concise but useful form, and utilize the interactive medium that the worldwide web offers for their retrieval. Downloaded databases and software for thermodynamic calculations are efficient for regular, expert users but are cumbersome for the occasional, less expert user. Retrieval of data through direct interaction with software on the server may be convenient for the occasional user, but may slow server responses significantly. The challenge is to develop interactive software for the potentially large set of non-expert users with sufficient versatility to allow complicated technical questions to be answered, sufficient speed to make the calculations efficient, and sufficient interpretation to allow the user to properly use the information.

A workshop on "Databases for Computational Thermodynamics and Kinetic Modeling" was organized. The approach of the workshop was to identify the database and information delivery tool needs of industry and education. The anticipated benefits from extended modeling and simulation capabilities are cost savings, improvements in environmental quality and energy conservation. Roadmaps were developed for how these needs can be met through expanded collaborative efforts in education, basic research and database development within the next decade.

The thermodynamic databases developed in this project were used to generate phase equilibria data on the web pages in the form of phase diagrams. In addition, the thermodynamic databases are available in the form of downloadable files which can be processed into customized output by user software or by specialized software developed by us and downloadable from our website.

The phase diagram website provides links to the NIST mechanical properties internet site allowing the user to examine the mechanical properties data that are available for the material.

The following information has been added on the site *www.metallurgy.nist.gov/phase/*:

- A link to the file with the thermodynamic 10 component database (Ni-Al-Co-Cr-Hf-Mo-Re-Ta-Ti-W) for superalloys with descriptions of liquid, γ (fcc) and γ' ($L1_2$) phases.
- A series of pages with binary phase diagrams for solder alloys. The binary systems are: Ag-Bi, Ag-Cu, Ag-Pb, Ag-Sb, Ag-Sn, Bi-Cu, Bi-Pb, Bi-Sb, Bi-Sn, Cu-Pb, Cu-Sb, Cu-Sn, Pb-Sb, Pb-Sn and Sb-Sn.
- A series of pages with ternary phase diagrams solder alloys with Sb. Each page contains a calculated liquidus projection for Sn-rich systems, enlargement of the Sn-rich corner, and a table of the invariant reactions in this system. The ternary systems are: Ag-Bi-Sb, Ag-Cu-Sb, Ag-Pb-Sb, Ag-Sb-Sn, Bi-Cu-Sb, Bi-Pb-Sb, Bi-Sb-Sn, Cu-Pb-Sb, Cu-Sb-Sn and Pb-Sb-Sn.
- Tutorial pages that illustrate the usage of phase diagram information. Examples are given for different cases with solidification following the lever rule equilibrium and Scheil path.
- Links to scripts for the simulation of DTA curves.

Future work will include the development of easy-to-use interfaces for the task-specific software that will be posted either for interactive use or downloads on the web site.

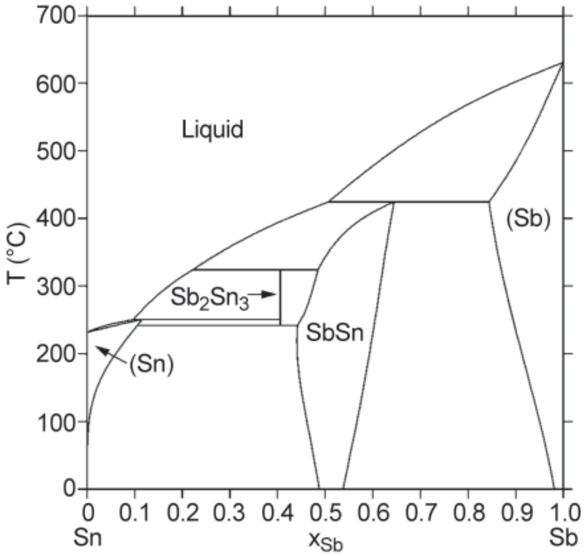


Figure 1: *Calculated Sb-Sn phase diagram.*

Contributors and Collaborators

W.J. Boettinger, R.J. Fields, J.E. Bonevich, K.-W. Moon

Mechanical Properties of Metals and Alloys on the Internet

With the increased use of the Internet, being able to electronically access critically evaluated data pertaining to the mechanical properties of materials has become more important to the U.S. industry. This information is required for the material selection or computer simulation using finite element methods during key stages of the design process. During this past year, we have concentrated in developing the necessary infrastructure to easily deliver the vast data generated or evaluated in the Metallurgy Division in a coherent searchable manner.

Richard J. Fields and Carlos R. Beauchamp

Mechanical properties are used to predict the performance of metallic components during fabrication and in service. There is a great abundance of mechanical properties data, but access to this data by traditional literature searching is a time consuming, inefficient, and costly process. More and more scientists and engineers representing the full range of U.S. industry, academia, and government agencies search for data electronically almost to the exclusion of print media. This project intends to provide a special site for NIST generated or evaluated data, a portal to other sources of data, and an easily adaptable interactive site that will address more precisely the needs of specific industrial communities.

To this end, collaboration between NIST and Granta Design Limited, United Kingdom, has yielded a materials property database that is in the pilot stages for access through the Metallurgy Division web homepages. Included in the database are:

- Mechanical and physical properties of solder alloys, including the results from three national consortia on lead-free solders for microelectronics applications;
- Mechanical and physical properties of solder joint intermetallics formed between tin and copper or nickel. Hardness and toughness of these alloys as a function of temperature as well as other room temperature properties are included;
- Mechanical property data forming the basis of constitutive equations for deformation of metals and alloys; and
- Deformation maps showing transitions in mechanisms with temperature, grain size, and other properties (Figures 1 and 2).

Collaboration is continuing with Professor H.J. Frost of Dartmouth to develop an online access to the high information density of deformation mechanism maps. These maps not only include most available data for a given material, but also provide constitutive equations that permit calculation of behavior in regions of stress and temperature of interest to the user but where no data exist. This combination of deformation maps and constitutive equations will be a powerful tool for scientists and engineers to model and quantify the effects of microstructure, fabrication processes and use conditions on mechanical performance.

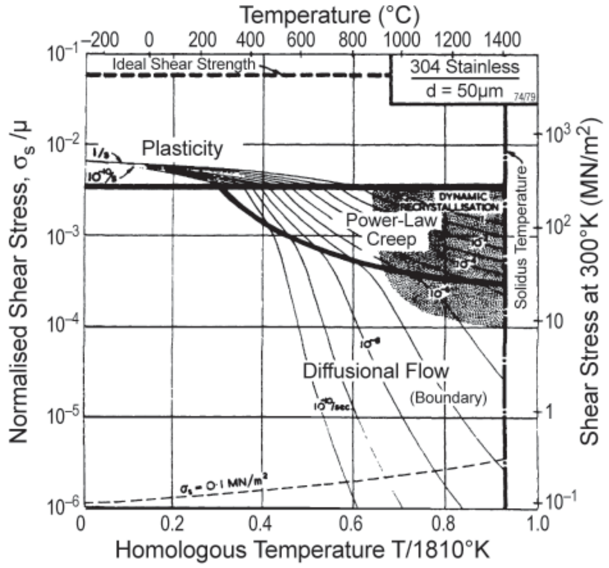


Figure 1: *Stress versus temperature map for 304 stainless steel with 50 µm grain size.*

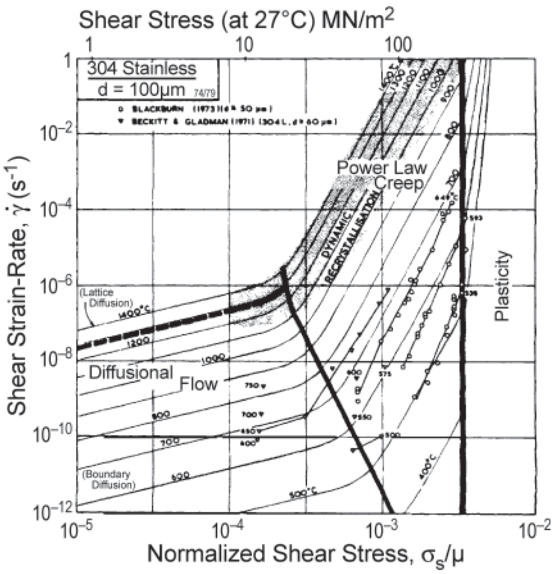


Figure 2: *Strain rate versus temperature map for 304 stainless steel with 100 µm grain size.*

Contributors and Collaborators

C.A. Handwerker, U.R. Kattner, J. Bonevich, R. Brown, H.B. Gates, S. Tobery (NIST/MSEL); H.J. Frost (Dartmouth College)

Electrodeposited Coating Thickness Standards

For over 50 years, NIST has been providing the coating industry with electrodeposited coating thickness Standard Reference Materials (SRMs). These standards are used for the calibration of instruments that measure coating thickness using magnetic methods. This year, the Metallurgy Division has extended their customary services of providing the standards and their periodic verification to include the preparation of a recommended practice guide for their proper use.

Carlos R. Beauchamp

The Electrochemical Processing Group has played an important role in the development of magnetic methods for the measurement of coating thickness. In the mid 1940's, research at this institution made possible the development of instruments for the measurement of magnetic coatings over non-magnetic substrates and non-magnetic coatings over magnetic substrates based on the magnetic attraction principle.

The instrumentation measured the force of attraction between a magnet and the magnetic material. It quickly became a principal tool in the measurement of the coating thickness due to the ease of use, simplicity of the method, and the wide range of coating/substrates that could be measured by the method. The involvement was not limited to the development of the technique since the Institution has been providing standards for the calibration of such instrumentation ever since the wide acceptance of the method.

Although the instrumentation has evolved since its first appearance and new magnetic techniques are now employed, the use of the standards has essentially stayed the same. The standards provided by NIST consist of pre-configured sets of electrodeposited copper over low carbon steel substrate coupons with the coating thickness ranging from 6 μm to 2000 μm. The coatings are overplated with chromium, and the total coating thickness is certified. The maximum expanded uncertainties for these standards are 2% of the mean coating thickness over the surface of the coupon.

Modern electronic gages have made the measurement extremely simple. The operator places a handheld probe in contact with three or four different standards, provides the certified values for the known coating thickness, and then proceeds to repeat the contact process on the location to be measured.

The simplicity of the process masks potential problems that will arise during the process of obtaining the measurement. Factors such as mismatch of the composition or thickness of the substrate between the known and the unknown, curvature of the part being measured, proximity to edges or other part non-uniformity, roughness of the deposits, or type of calibration curve applied over the span of thickness being measured are usually paid little attention, if any, during the process of measurement. Such problems will usually create confusion amongst our customers when they try to match the values certified in our standards.

To help them understand the extent of the effect of such factors over their measurement process, a publication has been prepared. The *NIST Recommended Practice Guide — Using Magnetic Methods for the Measurement of Coating Thickness* covers such issues by explaining the source of the effects and presents example data demonstrating the extent of the effects. Suggestions on how to account for such effects are presented.

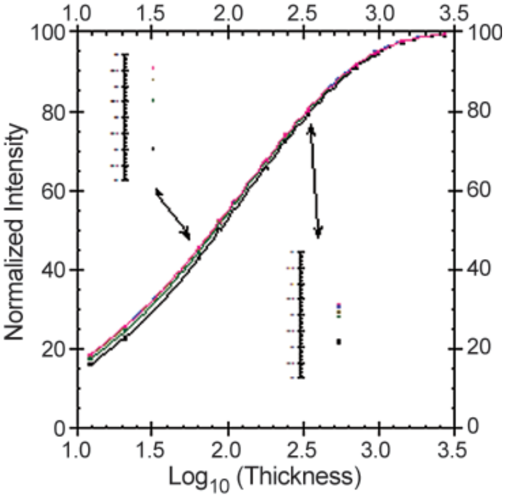


Figure 1: *Effect of the substrate on the measurement of the coating thickness: the thinner the coating, the higher the scatter of the collected data for the same foil thickness.*

Contributors and Collaborators

H.B. Gates, D.R. Kelley (NIST/MSEL); S.D. Leigh (NIST/ITL)

Forming of Lightweight Material for Automotive Applications

Automobile manufacturing is a materials intensive industry that involves about 10% of the U.S. workforce. In spite of the use of the most advanced, cost-effective technologies, this globally competitive industry still has productivity issues related to measurement science and data. Chief among these is the difficulty encountered in die manufacture for sheet metal forming. In a recent Advanced Technology Program-sponsored workshop (The Road Ahead, June 20–22, 2000, at USCAR Headquarters), the main obstacle to reducing the time between accepting a new design and actual production of parts was identified as producing working die sets. This problem exists even for traditional alloys with which the industry is familiar. To benefit from the weight saving advantages of high strength steel and aluminum alloys, a whole new level of formability measurement methods and data is needed, together with a better understanding of the physics behind metal deformation.

This program is meeting these industrial needs by developing: 1) standard formability test methods, 2) models for surface roughening and friction during stamping, 3) multiscale, physically-based constitutive laws, 4) models for anelasticity and springback prediction, and 5) measurements of texture and residual stress evolution. Our recently established sheet metal formability laboratory is now adding *in situ* X-ray equipment for measuring stress in sheet metal samples during multiaxial deformation. This laboratory permits us to investigate industrially important measurement problems in formability and pursue standard test methods for formability. The facility provides test samples of multiaxially deformed metal for other aspects of this program. For example, deformation-induced surface roughening of sheet metal is a poorly understood phenomenon that is highly relevant to industry. We are currently performing controlled experiments on multiaxially strained sheets to develop a surface roughening database and a generic model which industry has identified as a high priority need. The test methods and surface roughening projects were selected by the Industrial Liaison Office of NIST for a pilot survey aimed at obtaining comprehensive, non-biased feedback from industry. They received high scores on all aspects including industrial relevance and potential impact. On a more fundamental level, MSEL's advanced characterization capabilities (TEM, AFM, Synchrotron Radiation, NCNR) are being used to understand the basic dislocation patterning responsible for the observed behavior of metals. A predictive model based on percolation theory has been developed from the measurements and observations. All aspects of the research at NIST will impact our customers by improving the commercially available, finite element computer codes that are heavily used by this industry. A key element in the design of this program is that an insight or advancement gained in one area can be immediately used in a piecewise fashion in the design process, i.e., total success of the program is not required to have an impact. Other means of transferring this technology, such as through standardizing organizations and by direct interaction with industrial counterparts, are being pursued. While targeting the auto industry, our research will have extended applications to all other industries that employ metal forming in their production lines.

Contact: Lyle E. Levine

Plasticity, Fabrication Processes, and Performance

Inaccurate predictions of large strain plasticity under complex load histories such as those applied during industrially relevant processes are due to our limited understanding of the essential role played by microstructure. Significant advances in theoretical and modeling capabilities that include microstructure, and guided by experimental measurements and validation, are needed to shed new light on this problem. For example, NIST's OOF modeling program is severely limited by its inability to deal with plasticity. Remedying this is one of the principal challenges of this project.

Richard J. Fields

Diffraction provides a powerful means of very accurately measuring both microstructure and mechanical behavior in a way that provides insight simultaneously into both and offers particular opportunities for understanding plasticity. This project is implementing one or more plasticity models in OOF and devising critical experimental and computational benchmarks to validate OOF using the NCNR's neutron diffractometer to measure residual stress, texture, and elastic properties. Conventional x-ray sources are also being used where stress states measured at or near surfaces are important for understanding the behavior of materials or to compare with predictions. Synchrotron x-rays are used to deal with sub-surface residual stresses in the thin, highly-textured samples that result from simulated forming operations. Specifically, the following tasks are underway:

- Efforts to include plasticity in OOF and extend OOF to three-dimensional microstructures are being undertaken by continuing and expanding our current theory group meetings on these topics. Academic experts in this area are brought in to make sure our internal group is attacking these problems with the most up-to-date methods. Modification of the OOF program to include plasticity will involve the CTCMS staff currently working on OOF. The Metallurgy Division will supply them with algorithms for the code based on different types of plasticity.
- The effects of residual stresses, produced by heat treatment or initial machining, on distortion during subsequent machining steps are being established for prototype aluminum samples by neutron and x-ray diffraction to validate on-going calculations. (This part of the project includes collaborative contributions from MEL, Alcoa, and Boeing Corp.)

Once plasticity has been implemented in OOF, additional verification tests will be carried out against analytical models and ABAQUS. Validation tests will be carried out against benchmark experiments run at the NCNR and in the Metallurgy Division. An effort to include some simple 3-D character to OOF based on stereology may be included in this part of the research.

Accomplishments

- Installed a state-of-the-art goniometer on an x-ray source at NIST.
- Established a NIST access to residual stress measurement at the Advanced Photon Source and characterized the residual stress state in a standard Demeri cups supplied by Ford.
- Developed a research plan with Boeing and Alcoa to minimize machining distortion.
- Derived an analytical expression for the elastic behavior of polycrystalline materials to verify the performance of OOF.
- Collaborated with CTCMS staff to develop algorithms for a simple plasticity model for OOF.

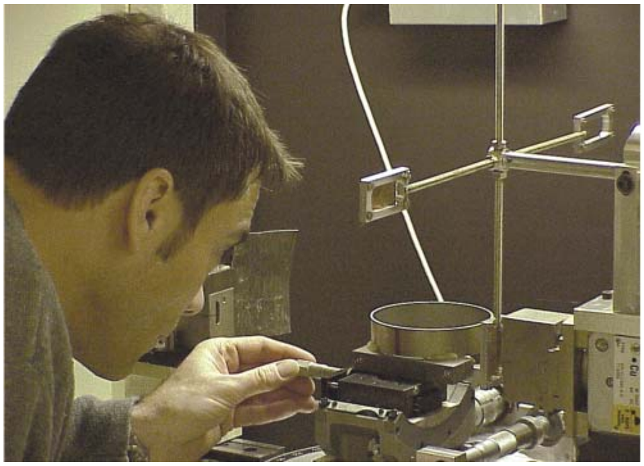


Figure 1: *Residual stress measurement in Demeri cup at Advanced Photon Source.*

Impact

This project has targeted a need expressed by numerous companies to extend OOF calculations into the plastic range. It is also responsive to the metal forming research needs of the auto industry, as well as Boeing, Alcoa and steel manufacturers with whom NIST currently collaborates. Improvements in predicting large plastic strain behavior under complex loading conditions will have significant benefits on product differentiation, time-to-market, and the cost of forming dies for U.S. products.

Contributors and Collaborators

Lyle Levine, Roland deWit (Metallurgy); Henry Prask, Thomas Herold, Vladimir Luzin (NCNR); Robert Polvani (MEL); David Bowden (Boeing); Edmund Chu (Alcoa); Robert Reno (University of Maryland); Lily Ma (Drexel)

Standard Test Method Development for Sheet Metal Formability

In order to meet the PNGV goals for fuel efficiency, the U.S. automotive industry is moving to lighter, high-strength materials for auto bodies. However, lack of experience in forming these materials translates into difficulty in making accurate dies for producing body parts. NIST's survey of the industry has found that accurate material properties, and a way to incorporate them into finite element models of sheet metal forming dies, is a critical need for the U.S. auto industry. This project seeks to develop new standard tests and metrology to accurately determine sheet metal mechanical response under forming conditions.

Timothy J. Foecke

In order for the U.S. automotive industry to be able to transition to new materials for formed sheet metal parts, the starting materials must be mechanically characterized under various forming conditions. These data can then be used as input for die design models. The Metallurgy Division has initiated a project to develop a sheet metal formability test, along with associated metrology, that can be standardized and easily used by industry to accomplish this task.

Springback is the elastic shape change to a part associated with the residual stresses that develop during the stamping process. This deviation in form complicates assembly and accurate fit-up resulting in a strong desire by the automotive industry to either avoid it or at least be able to predict its magnitude to account for it in die design.

In conjunction with members of the U.S. Council for Automotive Research (USCAR), efforts this year have concentrated on the Demeri cup springback test. The driving force for standardization of this test is its simplicity in terms of tooling, measurement techniques, and basic understanding of the data. In this test, a circular blank is drawn into a flat bottom cup. The sidewalls of the cup undergo a stretch-bend deformation path that introduces large residual hoop stresses. A ring is cut from the sidewall and split to produce a large and measurable elastic opening as shown in Figure 1. Insights gained in writing finite element codes to calculate springback in this simple body can then be applied to codes used to design more complex dies.

Figure 1: *Split ring from Demeri cup springback test.*

As part of a collaboration with Ford Motor Company, Fe- and Al-base samples are sent to NIST for inspection and measurement. While this test has several desirable attributes from a modeling perspective, such as axisymmetry, a number of experimental issues with this geometry have been found that complicate the analysis. As seen in Figure 2, the wall thickness varies around the perimeter of the cup. This was expected as the mechanical behavior of the sheet varies with respect to the rolling direction, affecting how the material flows into the tooling. In addition, it was also seen that the thickness varies along the height of the sidewall, consistent with the fact that more material is being drawn at the end of the process than the beginning.

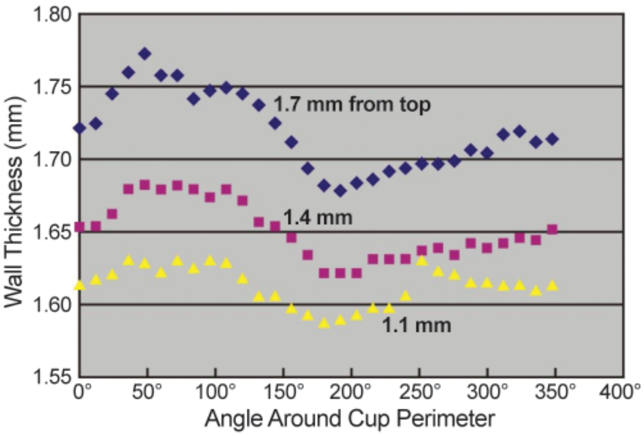


Figure 2: *Plot of wall thickness around perimeter of cup.*

Preliminary measurements of the stress in the ring prior to cutting have been made at the Advanced Photon Source and are consistent with initial predictions that the stresses are not linear through the thickness, as assumed by the models, but inflected in a complicated manner. This work is being expanded since it is of great interest to the forming industry.

Contributors and Collaborators

S.W. Banovic; T. Gnaeupel–Herold, H. Prask (856); M. Demeri (Ford); C. Xia (U.S. Steel); E. Chu (ALCOA)

Microstructural Origins of Surface Roughening and Strain Localizations

Existing data, measurements methods, and the basic understanding of metallurgical factors that influence friction, tearing, and surface finish during sheet metal fabrication are insufficient to meet the finite element modeling requirements of the automotive industry. This project approaches the resultant need by exploring the microstructural origins of the distribution of slip, surface roughening, and strain localization during plastic straining. Influence of initial material characteristics on the formability of Al and Fe base sheet metals as a function of biaxial deformation is the primary focus of the investigations.

Stephen W. Banovic

Replacement of conventional steel sheets by aluminum alloys and high-strength, low-alloy steels for various automobile closures is an effective means of reducing vehicle weight. However, wide-spread application of these metals by the automotive industry is limited due to formability issues related to a lack of experience with these new alloys. In addition, finite element modeling of new die designs has been hampered due to deficiencies in their inputs (existing materials databases) and the basic understanding of how metallurgical factors influence the resulting behavior of the material. Therefore, this project examines the underlying structure–property relationships associated with formability in an attempt to further numerical simulations that predict deformation behavior of materials.

The main concentration of this past year was to develop and/or improve upon the understanding of the measurement techniques being utilized. Past measurements of the strain-induced surface roughness were conducted using a contact stylus profilometer. This technique was found to be labor intensive and yielded limited data. A new laser confocal microscope has been obtained that will allow for the automated, rapid sampling of large areas, as well as produce line traces across an area of interest. It is expected that pre-programmed routines will soon be measuring samples at a high throughput to increase accuracy of the measurements and improve the statistics of the data.

Changes observed in the surface roughness due to plastic deformation have been correlated with the modification in crystallographic texture of the sheet. Three techniques are presently being used to measure this evolution, with each technique analyzing different sample volumes. The bulk measurement technique is Neutron diffraction (ND) which analyzes numerous pieces of sheet stacked on top of one another to produce a sample volume of approximately 125 mm^3. The method of X-ray diffraction (XRD) probes the top 2–3 grain layers over a 1 cm^2 area yielding data from roughly 5 mm^3. The final technique is electron backscatter diffraction (EBSD), which is used to analyze approximately 10 nm of the surface layer. Assessment of these different systems is currently underway as each technique has advantages and drawbacks. An example of these comparisons is show in Figure 1 for a 5xxx series aluminum alloy. These results indicate that the crystallographic textural development is similar at the surface of the sheet as it is throughout the bulk, even though constraint of the exterior grains is relaxed at the free surface. Further analysis is being conducted to quantify these comparisons.

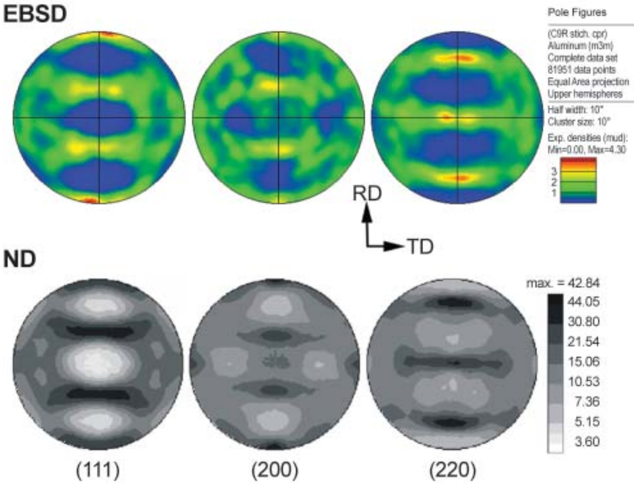


Figure 1: *Pole figures for AA5052-H32 deformed in a balanced biaxial mode to a strain level of 0.104.*

Future work will focus on surface roughness development and crystallographic texture evolution of samples deformed via multi-pass strain paths in attempts to simulate actual stamping operations. Transmission of this information to the technical community will be performed through the electronic databases of mechanical properties and material characteristics as a function of strain level made available on the NIST website. In addition, a workshop will be used to help introduce the work and identify the critical microstructural variables that are important to improving formability.

Contributors and Collaborators

T. Foecke, M.R. Stoudt, R.E. Ricker, D. Dayan; M.D. Vaudin, T. Gnaeupel-Herold, V. Luzin (NIST/ MSEL); W. Tong (Yale University); Y. Shim (University of Georgia)

Underlying Processes of Plastic Deformation

A substantial increase in the use of aluminum alloys and high-strength steels in automobiles would greatly increase fuel efficiency. The primary reason why this has not yet been done is a lack of accurate deformation models for use in designing the stamping dies. This project is developing a physically based model of plastic deformation using a combination of statistical physics approaches and advanced measurement techniques.

Lyle E. Levine

Plastic deformation of metals (as in cold rolling, stamping, drawing, extruding, and metal fatigue) is a topic of great importance to industries worldwide, and improvements in the basic technology would have a significant effect on our economy. As one example, stamped metal parts comprise about 1/3 of the weight of an automobile. If the currently used mild steel could be replaced by aluminum alloys or high-strength steels, weight could be reduced considerably, thus greatly increasing fuel economy.

The design of new metal products is often accomplished by computer simulation of the production process using empirically derived constitutive equations. Unfortunately, existing constitutive equations cannot accurately predict the material behavior, and many tryout and redesign steps are required. Another related difficulty is in the design of new alloys with improved formability characteristics. Currently, alloy design is done empirically with little understanding of how the various constituents affect the mechanical properties.

To address both of these issues, this project is focused on developing constitutive laws based upon the underlying physical processes that produce the observed mechanical behaviors in metal alloys. Such constitutive laws are inherently multi-scale since they must not only incorporate the atomic scale interactions in metal alloys but also contain transitions all the way from the atomistic to the macroscopic stress–strain behavior of bulk material.

Almost all of the changes in mechanical behavior that occur during deformation result from the transport of dislocations. The most difficult aspect of this problem is in the mesoscale, where large numbers of dislocations interact to form complex three-dimensional structures that both impede the motion of mobile dislocations and act as sources for new dislocations. Several years ago, we introduced a statistical physics model for this process called *strain percolation theory*. The model successfully described how dislocations propagate through dislocation structures but the connection to the smaller-length-scale physics remained tenuous.

In a major development over the past year, advances in our understanding of how strain is produced and transmitted during deformation has allowed us to make a firm connection to the smaller-length scales and to tie many apparently disparate phenomena together into a single theoretical framework that we call the *segment length distribution model*. The basic mechanism involves the interaction of the local and applied stress fields with the distribution of dislocation segments within dislocation walls. The evolution of this distribution directly determines the changes in the mechanical properties and it is strongly affected by the applied strain, stress, strain rate, temperature and alloy chemistry. Physical features such as vacancy concentration, diffusion rates, strain rates, and dislocation densities on the various slip systems can all be included directly. Although it is now clear how all of these features can be added to the model, much work remains to complete this.

The explicit incorporation of these (largely) atomistic-level details means that chemistry effects can be addressed directly. Such work should allow quantitative predictions to be made of the effects that different alloying elements would have on the mechanical behavior. The role of chemistry comes in naturally, and this is expected to be a significant new research topic in the next fiscal year.

A key observation that underlies most of our theoretical work is that slip is heterogeneous in both space and time. The strain percolation theory and segment length distribution model provide handles for addressing the time aspect and the spatial heterogeneity at short-length scales. An unresolved question is how the strain becomes localized (into slip bands) over larger length scales. This process is crucial to completing a physically-based constitutive law for single crystals. During the past year, we completed an experimental effort aimed at providing crucial input into our theory work on this topic. Numerous single-crystal Al samples were grown with different crystallographic orientations. After straining, the underlying dislocation structures were examined using transmission electron microscopy. Other identical specimens were strained incrementally in an atomic force microscope, and the resulting formation and evolution of slip lines and bands was measured as a function of strain and crystallographic orientation. Interpretation of these data is ongoing. Once the localization process is understood, we will have developed fully coupled models ranging from the atomistic scale up through the single crystal level.

Contributors and Collaborators

D. Kramer, D. Pitchure, M.F. Savage, R. Thomson; G.G. Long (852); Y. Shim (University of Georgia)

Anelasticity and Springback Predictability

Increased computing power coupled with finite element modeling methods has brought the prediction of springback and springback compensated die design within the reach of industry. In developing this technology, industry has identified areas where better measurement methods and data are required and, in some cases, where our scientific understanding of materials behavior is incomplete. One such case is the influence of plastic deformation on the mechanisms of anelastic recovery and springback. The objective of this project is to develop the fundamental understanding, test methods, and data required to predict this phenomenon.

Richard E. Ricker

A U.S. Council for Automotive Research (USCAR) Consortium on Springback Prediction has recently reduced the errors in finite element prediction of springback to the point where they consistently underpredict springback by about 20%. At a meeting of the consortia, NIST scientists pointed out that this consistent error could be eliminated by assuming that plastic deformation reduces the modulus of elasticity. This hypothesis created controversy among the consortium members. Since this debate concerned fundamental issues related to measurement methods, NIST has examined this issue and hypothesized that the modulus appears changed because plastic deformation stimulates anelastic relaxations that occur after unloading.

To determine if this hypothesis warranted further investigation, springback was measured using existing laboratory equipment at NIST. First, springback was measured with the NIST Rockwell hardness calibration machine and it was found that anelastic recovery increased springback by about 20% (Figure 1). Second, springback was measured during 3-point bend tests using a servo-hydraulic testing machine with similar results. It was, therefore, concluded that developing a better measurement of anelastic relaxations and data on the influence of large-scale plastic strain on anelastic recovery would enable industry to make better springback predictions.

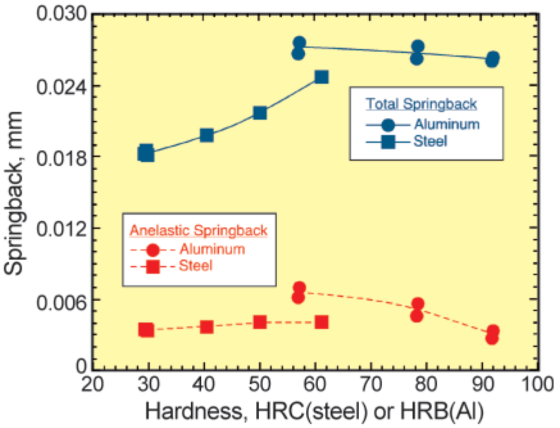


Figure 1: *The total springback and anelastic (non-linear) contribution in Rockwell hardness tests.*

To accomplish this objective, a dynamic thermal-mechanical testing machine was acquired in FY02. This equipment is capable of conducting mechanical tests at temperatures from −150 to 600°C and frequencies from 0.01 to 200 Hz with a 1 nm resolution of sample displacement. During FY02, our focus has been on developing experimental techniques for using this apparatus to study the influence of alloy composition and thermal mechanical treatment on: 1) complex modulus and 2) anelastic recovery. The first of these will be used to develop the fundamental understanding that will frame this effort while the second will be used to relate the fundamental understanding to industry relevant data. Once the scientific boundaries and measurement issues are understood, a standard test method for generating industry relevant data using a servo-hydraulic machine will be developed and the method and data distributed to the sheet metal forming industry.

An example of the influence of plastic deformation on anelastic behavior can be seen in Figure 2. In this figure, two samples of the same aluminum alloy that have received different thermal-mechanical treatments are compared and it can be seen that plastic deformation significantly increased anelastic behavior. Transmission electron microscopy of these samples confirmed the presence of a higher density of dislocations at grain boundary particles in the cold rolled sample.

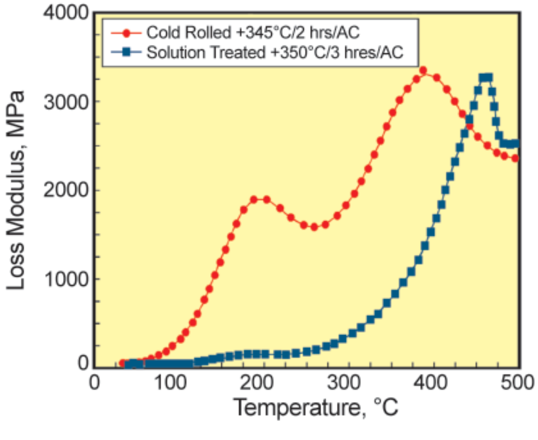


Figure 2: *Comparison of the imaginary or anelastic component of the complex modulus for deformed and undeformed aluminum samples.*

Contributors and Collaborators

D.J. Pitchure, D. Dayan, and the Springback Predictability Consortium (USCAR, Alcoa, Ford Motor Company, General Motors Corporation, DaimlerChrysler Corporation, Livermore Software Technology Corporation, U.S. Steel Corporation)

Materials for Micro- and Optoelectronics

U.S. microelectronics and related industries are in fierce international competition to design and produce smaller, lighter, faster, more functional, and more reliable electronics products more quickly and economically than ever before. At the same time, there has been a revolution in recent years in new materials used in all aspects of microelectronics fabrication.

Since 1994, the NIST Materials Science and Engineering Laboratory (MSEL) has worked closely with the U.S. semiconductor, component, packaging, and assembly industries. These efforts led to the development of an interdivisional MSEL program committed to addressing industry's most pressing materials measurement and standards issues central to the development and utilization of advanced materials and material processes. The vision that accompanies this program — to be a key resource within the Federal Government for materials metrology development for commercial microelectronics manufacturing — is targeted through the following objectives:

- Develop and deliver standard measurements and data;
- Develop and apply *in situ* measurements on materials and material assemblies having micrometer- and submicrometer-scale dimensions;
- Quantify and document the divergence of material properties from their bulk values as dimensions are reduced and interfaces contribute strongly to properties;
- Develop models of small, complex structures to substitute for, or provide guidance for, experimental measurement techniques; and
- Develop fundamental understanding of materials needed in future micro- and opto-electronics and magnetic data storage.

With these objectives in mind, the program presently consists of projects led by the Metallurgy, Polymers, Materials Reliability, and Ceramics Divisions that examine and inform industry on key materials-related issues. These projects are conducted in concert with partners from industrial consortia, individual companies, academia, and other government agencies. The program is strongly coupled with other microelectronics programs within government and industry, including the National Semiconductor Metrology Program (NSMP) at NIST. Materials metrology needs are also identified through industry groups and roadmaps including the International Technology Roadmap for Semiconductors (ITRS), International SEMATECH, the IPC-Embedded Passive Devices Taskgroup, the IPC Lead-free Solder Roadmap, the National Electronics Manufacturing Initiative (NEMI) Roadmap, the Optoelectronics Industry Development Association (OIDA) roadmaps, and the National [Magnetic Data] Storage Industry Consortium (NSIC).

Although there is increasing integration within various branches of microelectronics and optoelectronics, the field can be considered to consist of three main areas. The first, microelectronics, includes needs ranging from integrated circuit fabrication to component packaging to final assembly. MSEL programs address materials metrology needs in each of these areas, including, for example, lithographic polymers and electrodeposition of interconnects, electrical, mechanical, and physical property measurement of dielectrics (interlevel, packaging, and wireless applications), and packaging and assembly processes (lead-free solders, solder interconnect design, thermal stress analysis, and co-fired ceramics).

The second major area is optoelectronics, which includes work that often crosses over into electronic and wireless applications. Projects currently address residual stress measurement in optoelectronic films, and wide bandgap semiconductors. Cross-laboratory collaborations with EEEL figure prominently in this work.

The third area is magnetic data storage, where the market potential is already large and growing and the technical challenges extreme. NSIC plans to demonstrate a recording density of 40 times today's level by 2006. To reach these goals, new materials are needed that have smaller grain structures, can be produced as thin films, and can be deposited uniformly and economically. New lubricants are needed to prevent wear as the spacing between the disk and head becomes smaller than the mean free path of air molecules. MSEL is working with the magnetic recording industry to develop measurement tools, modeling software, and magnetic standards to help achieve these goals. MSEL works in close collaboration with the Electronics and Electrical Engineering Laboratory, the Physics Laboratory, the Information Technology Laboratory, and the Manufacturing Engineering Laboratory as partners in this effort.

Contact: Frank W. Gayle

Mechanism of Sn Whisker Growth from Electrodeposits

The electrodeposition of metallic alloys has been central to the growth of the electronics industry. This is largely due to the exceptional properties exhibited by electrodeposited material as well as the favorable economy of scale associated with electrodeposition processes. A technology important to electronics manufacturing is the electrodeposition of Sn-based coatings and surface finishes to guarantee solderability. With the rapid move to Pb-free solder surface finishes, new test methods are needed for predicting the tendency of such coatings to form Sn whiskers that can lead to catastrophic failures.

Christian E. Johnson, Maureen E. Williams, and Kil-Won Moon

In FY2001, the National Electronics Manufacturing Initiative (NEMI) Pb-Free Task Force, of which NIST is a member, identified a serious concern of OEMs, contract manufacturers, and component manufacturers with the conversion from Sn-Pb to Pb-free surface finishes for circuit boards and component leads. It is well known that the use of pure Sn protective surface finishes can cause serious problems: tin whiskers (1 mm diameter and several mm long) can grow from the plated tin surface and cause electrical shorts and catastrophic failure. Historically Pb was added to Sn plate to prevent whisker growth, and, thus, the "whisker problem" disappeared. With the rapid move to environmentally-friendly Pb-free assemblies, the microelectronics industry must remove Pb from the surface finishes. For many applications, an electroplated Sn-based surface finish remains a preferred surface for ease of processing. However, the growth of whiskers is currently a perilous drawback.

Based on these needs, this NIST project is focusing on: 1) understanding the effect of alloying elements other than Pb on the tendency for whisker formation, 2) developing techniques to separate possible physical and microstructural factors affecting whisker formation, and 3) assisting the NEMI Standardization Technology Integration Group (TIG) with both test development and understanding the root causes of whisker formation. The Sn-Cu system was chosen as the most versatile for electroplating, since it is compatible with Sn-3.9Ag-0.6Cu and Sn-0.7Cu, the Pb-free solders selected as the new national standard alloys by NEMI for reflow soldering and for wave soldering, respectively.

Whiskers are generally believed to grow to relieve residual stress in electroplated Sn. However, the origin of this stress has not been determined definitively. Therefore, as a starting point, we focused on the relationship of microstructural change and whisker formation as a function of Cu additions. Increased Cu content reduced the grain size of the Sn deposit from $0.65\,\mu m$ to $0.2\,\mu m$. Furthermore, Cu in deposits forms Cu_6Sn_5 intermetallic compounds (IMC) at the Sn grain boundaries. In the absence of Cu additions, no whiskers were observed after one year of room temperature aging. However, with Cu additions, whiskers were observed within two days increasing to a density of $50/mm^2$ after one year for the highest Cu levels.

Our current hypotheses are that a smaller grain size produces a higher level of intrinsic stress and that the presence of IMC particles at the grain boundaries may prevent relaxation of the stress. As a consequence, the stress level in the Sn-Cu deposits is relieved through whisker growth. To investigate this idea, cantilever beam test coupons were made from phosphor bronze and a commercial bright electrolyte. Using Stoney's Equation, an average planar stress of the deposited film was calculated from the deflection of the beam as a function of time. Preliminary results of pure Sn and Sn-Cu deposits indicated that the presence of the IMC particles in the Sn-Cu deposits inhibited stress relaxation. The compressive stress in the pure Sn deposit went from an initial level of 14 MPa to zero after four days. In contrast, the initial compressive stress in the Sn-Cu deposit was 32 MPa and after 100 days was still at 21 MPa. Whiskers were present after four days on the Sn-Cu sample, but after 100 days, the pure Sn sample was still whisker-free.

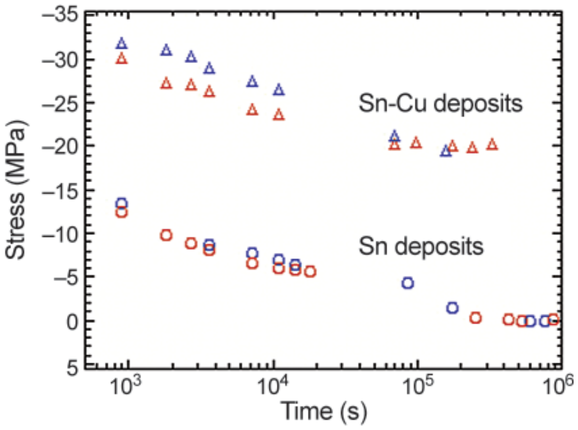


Figure 1: *Calculated stress levels with and without Cu additions.*

NIST is providing leadership in two NEMI whisker projects: identifying the fundamental growth mechanism and developing an accelerated test method. Our goal at NIST is to provide an understanding of the fundamentals of the whisker formation, which will ensure that the test developed by the NEMI group will have widespread applicability.

Contributors and Collaborators

W.J. Boettinger, G. Stafford (NIST); R. Gedney, I. Boguslavsky, P. Swaminath (NEMI project members)

Superconformal Film Growth: Measurements and Modeling

State of the art manufacturing of microelectronic devices relies on superconformal deposition of copper for on-chip interconnects. Superfilling of trenches and vias results from the interplay of rate inhibiting and accelerating adsorbates. NIST has recently identified the mechanism that explains "bottom-up" filling of submicrometer features. A quantitative capability for predicting the influence of adsorbates on superconformal film growth has been demonstrated. The mechanism has also been shown to apply to the electrodeposition of elements beyond copper, as well as CVD processing.

Thomas P. Moffat and Daniel Josell

The mechanism of superfilling or "bottom-up" filling of submicrometer features has been explained. The chief tenets are: a) the deposition rate is proportional to catalyst coverage and b) the catalysts "floats" or remains segregated at the interface during film growth. Superfilling follows as a natural consequence of these stipulations. Namely, the catalysts coverage increases (decreases) as the local surface area decreases during deposition, thereby giving rise to "bottom-up" filling and a bright surface finish.

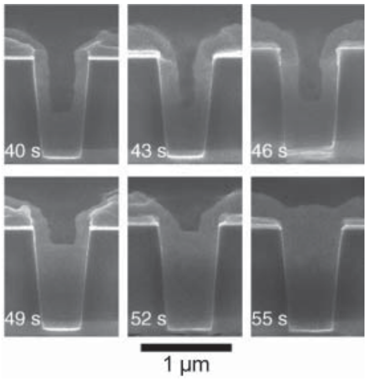


Figure 1: *"Bottom-up" filling of vias with silver.*

Quantitative description of the curvature enhanced accelerator coverage (CEAC) mechanism enables the simulation of feature filling. Three different electrode shape-change algorithms have been developed: 1) a simple model based on the solution of a single first-order differential equation, 2) a parameterized interface tracking code, and 3) a level set model, which incorporates a rigorous description of all concentration fields. Good agreement was found between these formalisms and feature filling experiments. A summary of the "simple model" simulations for filling trenches of variable aspect ratio as a function of applied potential and catalyst concentration is shown in Figure 2.

The generality of the CEAC mechanism has been verified by demonstrating superfilling of metals other than copper, i.e. silver electrodeposition from an alkalin electrolyte, as well as the first quantitative predictions of superfilling by iodine catalyzed chemical vapor deposition (CVD).

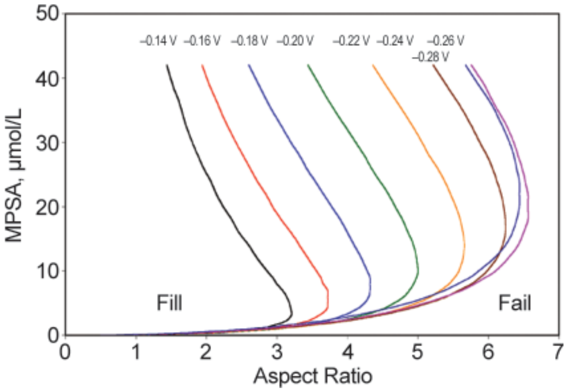


Figure 2: *Feature fill/fail bondaries as a function of processing parameters: catalyst concentration, etc.*

All kinetic parameters were determined from voltammetric (i-V) and chronoamperometric (i-t) experiments performed on planar substrate. Correlation between the reactivity and catalyst coverage was determined by surface analysis following metal deposition or, alternatively, by dosing the surface with a prescribed quantity of catalyst prior to the metal deposition experiment. The second scheme not only substantiates the CEAC mechanism but may also be implemented in manufacturing in order to circumvent the challenging control issues associated with catalyst consumption during electrolyte aging.

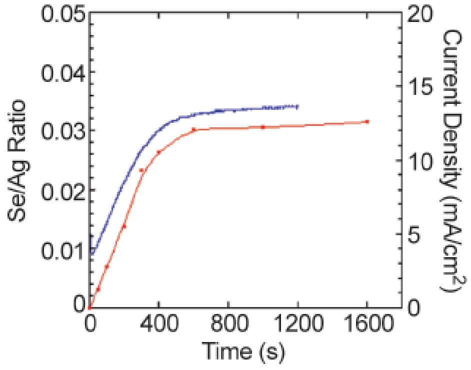


Figure 3: *A one-to-one correlation between catalyst coverage (red) and the deposition rate (blue).*

Contributors and Collaborators

D. Wheeler, J. Bonevich, W. Egelhoff, G. McFadden (ITL); S. Coriell, B. Baker, C. Yang, L. Richter, S. Robertson (CSTL); J. Mallett, C. Witt (International SeMaTech); B. Melnick, M. Freeman (Motorola); S.G. Pyo (Hynix Semiconductor)

Solder and Solderability Measurements for Microelectronics

Solders and solderability are increasingly tenuous links in the assembly of microelectronics as a consequence of ever-shrinking chip and package dimensions and the international movement toward environmentally-friendly, lead-free solders. Through collaboration with the NEMI Pb-Free Assembly Project, we are providing the microelectronics industry with measurement tools, data, and analyses that address national needs in the implementation of lead-free solders. We also work with industrial standards organizations to provide measurement methods and guidance for integration of lead-free solders and new component types into assembly processes.

Maureen E. Williams, William J. Boettinger, Carol A. Handwerker, Ursula R. Kattner, and Frank W. Gayle

The U.S. microelectronics industry has clearly articulated the measurement needs for Pb-free solders and for solderability and assembly. For example, the urgency for materials data for Pb-free solders has been specified in the 1997 IPC, 1999 ITRS, 2000 NEMI, and 2000 IPC Lead-Free Solder Roadmaps. The pressure from the Japanese consumer product market and from the EU to produce lead-free microelectronics continues to increase. In addition, the lack of understanding and control of current standard solderability measurements has inhibited the development of improved measurements necessary for new solders and for new packaging schemes. These industrial needs are addressed through this NIST project.

Since 1999, NIST has served a major role in the NEMI Pb-Free Assembly Project to identify and move Pb-free solders into practice. Last year, NIST held a workshop cosponsored by NEMI, NSF, and TMS, on Modeling and Data Needs for Lead-Free Solders. The report from this workshop is serving as a roadmap for research on the reliability of lead-free solders. In FY2002, the NEMI Lead-free Task Force and the National Institute of Standards and Technology (NIST) have worked together to respond to the identified needs by:

- Identifying the most important lead-free solder data for the microelectronics community;
- Developing "a guide to recommended practices" for measuring the mechanical, thermal, electrical and wetting properties of lead-free solders. This document is being distributed to all interested parties through the NEMI and NIST websites and through NIST in hard copy form;
- Gathering into a single database existing physical and mechanical property data that have been developed by researchers around the world;
- Critically reviewing existing materials property data for the most important alloys for use in finite element analyses; and
- Providing a list of literature references on alloys, processing, reliability, environmental issues, and components for assisting in the implementation of lead-free solders.

In a second major activity with the NEMI Lead-Free Assembly Project, NIST completed the microstructure-based failure analysis of thermally-cycled assemblies as part of the project's full-scale reliability trials with the new national standard Pb-free solder. The NEMI Final Report will be issued in early FY2003.

NIST is also working in collaboration with the IPC Standards Committees (most closely with members from Celestica, Lucent, Raytheon, Rockwell, and Shipley-Ronel) to establish reproducible solderability test standards for board assembly. Activities include: 1) providing benchmark experiments for the wetting balance tests to predict on-line solderability for a wide range of surface finishes, lead materials, and solder alloys; 2) developing a "best practice" for globule solderability test for small components and pads; and 3) evaluation of the effect of component lead geometery on industrial solderability tests.

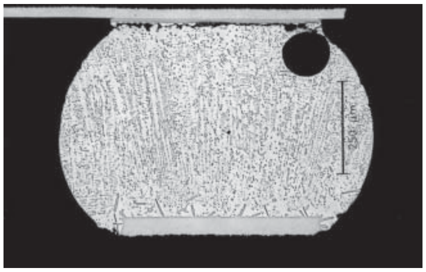


Figure 1: *Metallographic cross-section of a lead-free SnAgCu solder joint showing fracture in the solder adjacent to the interface with the component following accelerated thermal cycling. Failure location is the same as for Sn-Pb eutectic solder, which this alloy is replacing as a standard alloy.*

Highlights

- Sources of uncertainty have been established for wetting balance solderability tests leading to increased repeatability and reproducibility of tests.
- Recent flux studies performed at NIST led to a change in test procedures for the IPC/EIA/JEDEC J-STD 002 solderability standards.
- Research at NIST helped to separate the role of solder melting temperatures from solder paste wetting dynamics and the effect of air reflow.

Contributors and Collaborators

L.C. Smith (NIST); K.-W. Moon (University of Maryland); D. Napp (National Center for Manufacturing Sciences and associated consortium members); R. Gedney (NEMI Lead-Free Task Force and associated consortium members)

Magnetic Properties and Standard Reference Materials

Users of magnetic materials, including the recording industry, the permanent magnet industry, and the manufacturers of electric motors and transformers of all types, need standard reference materials (SRM's) to calibrate instruments used to measure the critical magnetic properties of their starting materials. The magnetic materials group is in the process of developing such standards. Methods for improving the efficiency and accuracy of measuring and characterizing magnetic materials of industrial importance, including measurement of magnetic susceptibility over wide frequency ranges, are also under investigation.

Robert D. Shull and Robert D. McMichael

In collaboration with scientists from universities, industry, and other Divisions at NIST, magnetic materials important to the scientific and industrial communities are prepared and methods for the improved measurement of their properties are developed. Standard Reference Materials for the calibration of existing and planned instruments used in the measurement of magnetic properties are developed and produced. An equally important parameter to know how to measure is time dependence of magnetization. Consequently, methods for the characterization of accommodation and aftereffect in magnetic recording and permanent magnetic materials are developed. Models are also developed for determining the most efficient methods to fully characterize the hysteresis and magnetostriction in magnetic materials.

Commercial instruments for the measurement of magnetic properties are relative instruments that rely on known samples for their calibration. To produce standard samples for such instruments, an absolute magnetometer was developed and assembled at NIST. A picture of this instrument is shown below.

Figure 1: *Absolute magnetometer.*

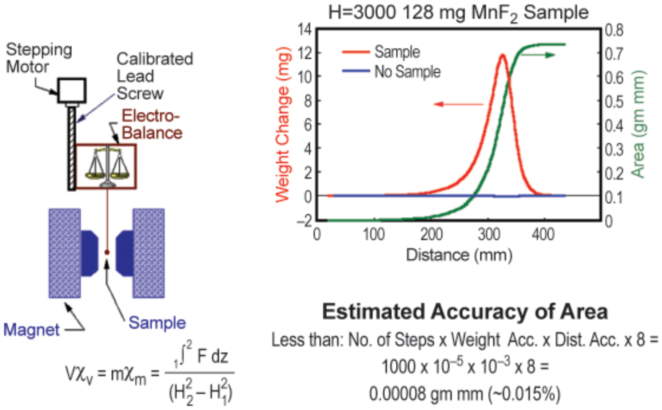


Figure 2: *Thorpe-Sentfle Method for Absolute Susceptibility Measurement.*

Prior to FY02, two SRM's were issued: a nickel sphere (SRM 772a) and a nickel disc (SRM 762). The measurements for the complete series of magnetic SRMs are made using the Thorpe–Sentfle method shown above. This technique has the advantage of not requiring knowledge of the field gradient anywhere in the apparatus. As that is the largest source of error, higher accuracy is possible.

We measure the susceptibility by physically moving the sample to various positions from the field center to some distance outside of the magnet measuring the magnetic force and then integrate that force vs. distance relationship.

Two new SRMs were developed this year. The first was a 1 mm diameter yttrium iron garnet (YIG) sphere for use in calibrating the more sensitive ranges of magnetometers (SRM 2853). In addition, it will be useful in calibrating very sensitive instruments such as alternating gradient magnetometers and SQUID magnetometers. Because of its high resistivity, the yttrium iron garnet sphere should also be useful for calibrating magnitude and phase in alternating current magnetometers. The second SRM is a platinum cylinder paramagnetic susceptibility standard (SRM 764a). This will be useful in calibrating the zero field point and linearity of magnetometers due to its paramagnetic nature, and it will also be useful for calibrating the field scale after the moment scale has been calibrated.

Contributors and Collaborators

A.J. Shapiro, R.V. Drew; S.D. Leigh (ITL); Industrial and academic collaborators: L.J. Swartzendruber, D.E. Matthews, G.E. Hicho, L.C. Smith, L.H. Bennett, E. Della Torre (George Washington University)

Magnetic Properties of Nanostructured Materials

In the past decade, there has been a remarkable improvement in the technology for materials preparation resulting in present day's capability of controlling morphology and features at the nanometer level. In magnetism, such control allows the fabrication of nm-thick composite materials of dissimilar magnetic behavior, leading to materials with novel bulk magnetic character and unusual properties. We are providing materials metrology necessary for U.S. industry to understand the behavior of these new materials and take advantage of the novel properties.

Alexander J. Shapiro and Robert D. Shull

Greater information storage on recording discs is being accomplished by reducing the size of the regions in which information is stored down to nanometer sizes. Unfortunately, when those regions become too small, the material ceases to be ferromagnetic (FM) and, instead, becomes superparamagnetic and no longer retains magnetic information. In order to exceed the so-called "superparamagnetic limit," the recording industry has recently introduced magnetic media containing two layers of a ferromagnet separated by a sub-nanometer thick layer of Ru. In this structure, the thickness of the nm-diameter regions has been effectively increased by providing magnetic coupling between the two ferromagnetic layers via the in-between Ru. Consequently, the volume of the element has been maintained large, even though the lateral dimensions of the recording "bit" have been decreased, thereby enabling retention of the ferromagnetic state. However, for this new type of media, it is unknown how long information will be retained in those "bits" and what sort of fields are necessary for reversing their magnetization. We have addressed this problem by imaging the magnetic domains in this new type of media using the magneto-optic indicator film (MOIF) technique developed in our laboratory (Figure 1).

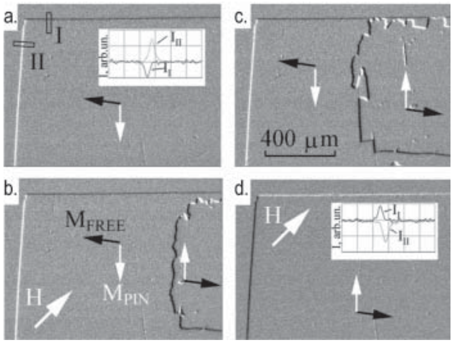


Figure 1: *MOIF image of the remagnetization process of a Co/Ru/Co homogeneous structure containing pinholes in the Ru in a field oriented along the total magnetization vector. (a) :$_o$H = 0 mT after magnetization in a field of +60 mT; (b) :$_o$H = –9.4 mT; (c) :$_o$H = –9.4 mT after a 5 sec. wait; (d) :$_o$H = -13.0 mT. The inserts in (a) and (d) show the intensity change of the MO signal.*

The first conclusion from the MOIF observations was that, surprisingly, the magnetization vectors in the two FM layers in this 3-layer structure were not colinear as originally assumed. In Figure 1, the lack of colinearity is seen by the 100 degree angle between the magnetization vectors (one white and the other black) of the two FM layers. As a consequence of this non-colinearity, the magnetization reversal mechanism now involves the cooperative behavior of both Co layers simultaneously, leading to different coercive fields and switching speeds. Figure 2 (e-h) shows that this non-colinearity is due to the presence of pinholes in the 0.5 nm thick Ru.

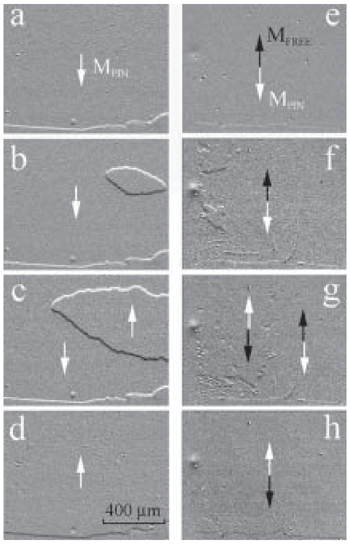


Figure 2: *MOIF image of the remagnetization process of a Co/Ru (a-d) and a Co/Ru/Co (e-h) thin film containing no pinholes in a field oriented along the total magnetization vector. H is directed vertically in the figure at increasing magnitude from 4 mT to 4.8 mT (a-d) and from 2 mT to 54 mT (e-h).*

For the Co/Ru/Co multilayer with no pinholes, the two FM layers have magnetization vectors which are colinear. With pinholes present, the greater their number, the greater their effect on the magnetic spin misalignment shown in Figure 1. Since most sub-nanometer thin films contain pinholes, these results clearly demonstrate the importance of knowing the effect of these defects. One of the ramifications of the non-colinearlity is the presence of time dependence in the coercivities of the stored information, a particularly deleterious situation. Information safely stored now may not be safely stored tomorrow. Two papers have been published presenting these results and a third is in progress to clarify the situation.

Contributors and Collaborators

Alexander J. Shapiro, Robert D. Shull, Robert D. McMichael, William F. Egelhoff (NIST); Valerian I. Nikitenko (Johns Hopkins University); Vladimir S. Gornakov (ISSP, Russian Academy of Sciences, NIST)

Nanomagnetodynamics

For GHz data rate hard drives, magnetic memory chips and other high-frequency magnetic devices, magnetization damping will be an important factor affecting performance. Another consequence of damping is thermal fluctuations that cause sensor noise and data loss in media. We provide industry with: 1) an improved understanding of magnetic damping mechanisms, 2) improved magnetic damping measurements and standards, and 3) data and methods for controlling magnetic damping in technically relevant materials.

Robert D. McMichael

This project is concerned with the metrology and mechanisms of magnetization damping, a process where magnetic energy is dissipated as the magnetization comes to equilibrium. The same mechanisms that allow damping also allow thermal energy to cause magnetization fluctuations that cause noise in sensors such as disk drive read heads and data loss in recorded media. Damping mechanisms are recognized as being important both for GHz data rate writing and reading processes and for long-term stability of stored data. A convenient measurement of damping is the ferromagnetic resonance (FMR) linewidth, a measurement that is complicated by the presence of inhomogeneities.

In FY2002, our accomplishments include: 1) a very successful model of ferromagnetic resonance in inhomogeneous films (see highlight), 2) demonstrations of the effects of intentional defects, 3) measurements of damping in thin magnetic metal films by spin transport into normal metals, and 4) measurements of the very low damping in high moment, soft materials under development for read heads.

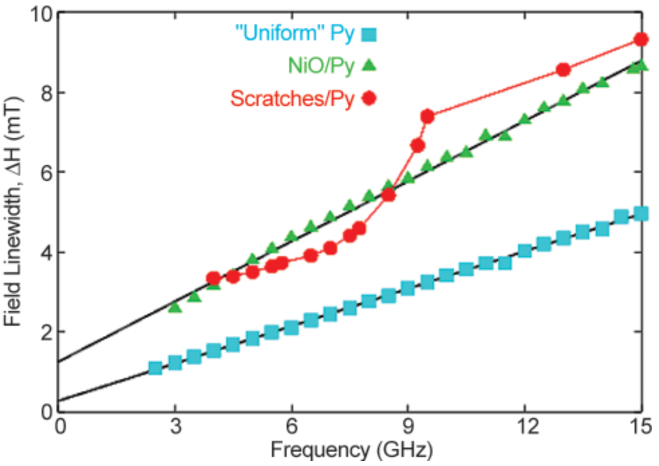


Figure 1: *Increased FMR linewidth resulting from intentionally-created defects created to clarify the effects of nanoscale defects on FMR damping measurements. Our modeling describes the effects of the random coupling to the polycrystalline, antiferromagnetic NiO.*

We have measured the intrinsic linewidth of Permalloy films, and we have found that it follows one of several proposed phenomenological forms. This data has been very valuable to theorists working on physical damping mechanisms.

One novel physical damping mechanism is damping via spin-polarized electron transport. It had been shown elsewhere that additional damping can be created by polarized electrons propagating into Pt or Pd surface layers. We have shown that the enhanced damping can be achieved with as little as 0.5 nm of Pt, and we have shown that the effect is substantially reduced by a Cu spacer between the Permalloy and Pt that is as thin as 0.5 nm. The abrupt decrease with a thin Cu spacer suggests that the damping enhancement has a contact component in addition to the spin transport component.

In FY2002, four papers related to this project were published, five contributed talks presented and three invited talks given at Seagate Research, U.C. San Diego, and a National Storage Industry Consortium meeting, and two more invitations have been received to speak at the 47th annual MMM conference in November 2002.

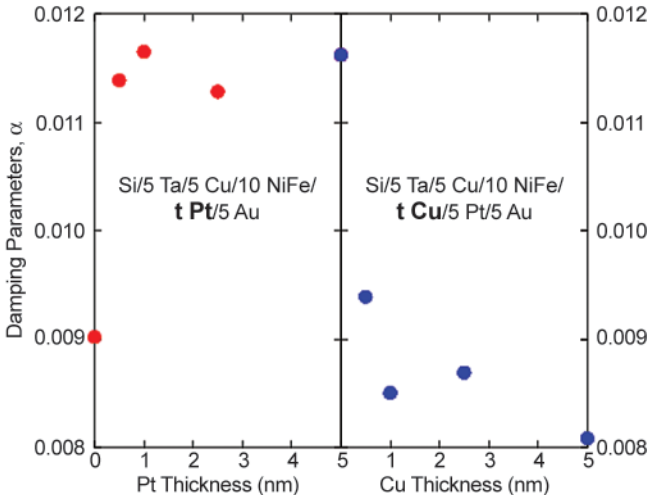


Figure 2: *Effect of Pt overlayers on damping in Permalloy films. The effect shows how spin polarized electron transport across the interface contributes to damping.*

Contributors and Collaborators

R.D. McMichael, A.B. Kunz, D.J. Twisselmann, A.P. Chen, W.F. Egelhoff (Metallurgy Division, MSEL); S.E. Russek (EEELM); E. McHenry, H. Okumura (Carnegie Mellon University)

New Materials for Ultra-High Density Data Storage

The objective of this program is to provide assistance to U.S. companies in the ultrahigh density data storage industry, which includes such products as hard disk drives and magnetoresistive random access memory chips. Our work provides U.S. companies with significant competitive help by investigating the scientific issues underlying the manufacturing process. Often, this scientific understanding will point the way to improved manufacturing processes. One such example is illustrated in the figures below.

William F. Egelhoff, Jr.

Hard disk drives play a crucial role in the information revolution. The World Wide Web is stored on millions of hard disk drives around the world. The exponential growth of the Web has depended on the exponential growth in hard disk storage capacity. Maintaining these exponential growth rates is one of the great challenges of the information age.

Today, giant magnetoresistance (GMR) is the current technology used for read heads in hard disk drives. It is unrivaled in its ability to read sub-micron-sized bits at gigahertz frequencies. However, the time is not far off when technologies better than GMR will be needed to maintain the historical exponential growth rates in storage density.

Our aim is to assist the U.S. companies that are developing these new technologies. One promising new technology is magnetic tunnel junctions (MTJs). MTJs are magnetic thin films with a typical layer structure of $Co/Al_2O_3/Co$. Electrons tunnel from one Co layer to the other through the Al_2O_3. One problem with MTJs is that they are not highly reproducible.

To understand the origin of this problem, NIST began a series of measurements at the Magnetic Engineering Research Facility (MERF) to determine the fundamental growth mechanisms in MTJ fabrication. MERF is a unique facility specifically designed to study surface and interface effects occurring during the growth of magnetic thin films for ultrahigh density data storage applications. The results at MERF identified interdiffusion at the Al/Co interface as a problem in the growth of MTJs, as illustrated in Figure 1.

When the Al is oxidized to make Al_2O_3 some of the Al remains in metallic form in the Co. The extent of the interdiffusion is highly susceptible to small changes in experimental conditions. As a result, nominally identical MTJs exhibit a lot of scatter in their performance data, as illustrated in Figure 2.

NIST demonstrated at MERF that oxidizing two atomic layers of the Co surface prior to the Al deposition provided an excellent diffusion barrier and that the Al reduced the Co oxide back to Co metal. NIST transferred this technology to Read-Rite, which found greatly improved manufacturing uniformity for MTJs and an improved magnetoresistance when this approach was used.

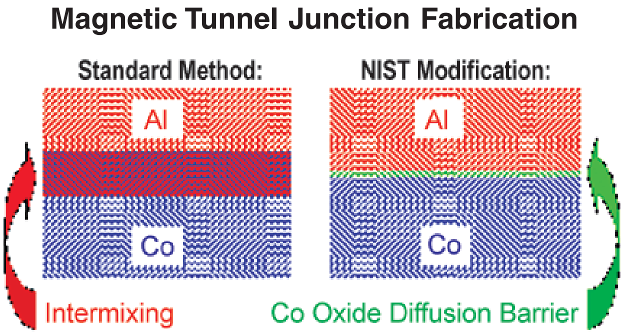


Figure 1: *An illustration of the intermixing that occurs in the standard method of MJT fabrication when Al is deposited on Co and the NIST modification using a thin Co oxide diffusion barrier to prevent the intermixing.*

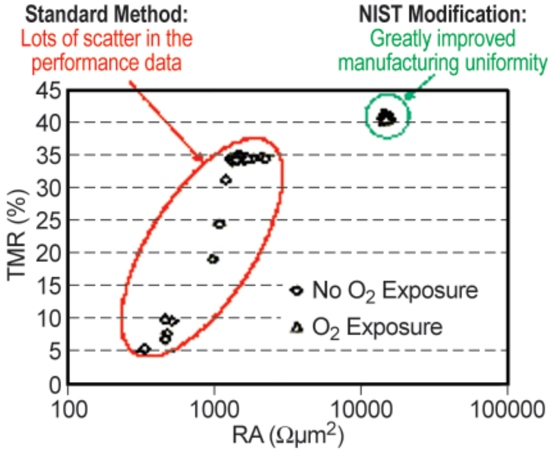


Figure 2: *Read-Rite Corp. data on magnetic tunnel junctions.*

> *"The results were amazing. The scattered data collapsed into a single point."*
>
> ***Dr. H.C. Tong***
> Director of Advanced Read-Head Research, Read-Rite Corp.

Contributors and Collaborators

W.F. Egelhoff, Jr., R.D. McMichael (NIST/MSEL); M.D. Stiles (NIST/Physics); 6 U.S. Corporations, the Naval Research Laboratory, 7 U.S. Universities, and 13 International Universities

Materials Property Measurements

This program responds both to MSEL customer requests and to the DOC 2005 Strategic Goal of "providing the information and framework to enable the economy to operate efficiently and equitably." For example, manufacturers and their suppliers need to agree on how material properties should be measured. Equally important, engineering design depends on accurate property data for the materials that are used.

The MSEL Materials Property Measurement Program works toward solutions to measurement problems, on scales ranging from the macro to the nano, in four of the Laboratory's Divisions (Ceramics, Materials Reliability, Metallurgy, and Polymers). The scope of its activities goes from the development and innovative use of state-of-the-art measurement systems, to leadership in the development of standardized test procedures and traceability protocols, to the development and certification of Standard Reference Materials (SRMs). A wide range of materials is being studied, including polymers, ceramics, metals, and thin films (whose physical and mechanical properties differ widely from the handbook values for their bulk properties).

Projects are directed to innovative new measurement techniques. These include:

- Measurement of the elastic, electric, magnetic, and thermal properties of thin films and nanostructures (Materials Reliability Division);
- Alternative strength test methods for ceramics, including cylindrical flexure strength and diametral compression (Ceramics Division); and
- Coupling micromechanical test methods with failure behavior of full-scale polymer composites through the use of microstructure-based object-oriented finite element analysis (Polymer Division in collaboration with the Automotive Composites Consortium).

The MSEL Materials Property Measurement Program is also contributing to the development of test method standards through committee leadership roles in standards development organizations such as ASTM and ISO. In many cases, industry also depends on measurements that can be traced to NIST Standard Reference Materials (SRMs). This program generates the following SRMs for several quite different types of measurements.

- Charpy impact machine verification (Materials Reliability Division);
- Hardness standardization of metallic materials (Metallurgy Division);
- Hardness standardization and fracture toughness of ceramic materials (Ceramics Division); and
- Supporting the Materials Property Measurements Program is a modeling and simulation effort to connect microstructure with properties. The Object-Oriented Finite-Element (OOF) software developed at NIST is being used widely in diverse communities for material microstructural design and property analysis at the microstructural level.

In addition to the activities above, the Materials Reliability, Metallurgy, Ceramics, and Polymers Divisions provide assistance to various government agencies on homeland security and infrastructural issues. Projects include assessing the performance of structural steels as part of the NIST World Trade Center Investigation, advising the Bureau of Reclamation (BOR) on metallurgical issues involving a refurbishment of Folsom Dam, advising the Department of the Interior on the structural integrity of the U.S.S. Arizona Memorial, advising the U.S. Customs Service on materials specifications for ceramics, and advising the Architect of the Capitol on repair procedures for cracks in the outer skin of the Capitol Dome.

Contact: Samuel R. Low

Hardness Standardization: Rockwell, Vickers, Knoop

U.S. industry needs to be able to make measurements that are traceable to national standards and compatible with the measurements made in other countries. This need is being emphasized by the requirements of quality standards such as ISO 17025. For the measurement of hardness, NIST is meeting this need by standardizing U.S. national hardness scales, producing hardness reference standards, and providing assistance and guidance to U.S. industry through national and international standards activities.

Samuel R. Low, Christian E. Johnson, James L. Fink, and David R. Kelley

Hardness is the primary test measurement used to determine and specify the mechanical properties of metal products. The Metallurgy Division is engaged in all levels of hardness standards activities to assist U.S. industry in making measurements compatible with other countries around the world. These activities include the standardization of the national hardness scales, development of primary reference transfer standards, leadership in national and international standards writing organizations, and interactions and comparisons with U.S. laboratories and the National Metrology Institutes of other countries.

International Activities

At the international level, we are participating in the Working Group on Hardness (WGH) under the International Committee for Weights and Measures (CIPM) (Figure 1). The primary goal is to standardize hardness worldwide. With NIST serving as secretary of the WGH, this year's WGH work has included an initial effort to better define the Rockwell hardness test procedure used by National Metrology Institutes (NMIs). Other international activities include: heading the U.S. delegation to the International Organization for Standardization (ISO) TC 164/SC 3 committee on hardness testing of metals, which oversees the ISO hardness test method standards; acting as the U.S. representative to the International Measurement Confederation (IMEKO) TC5 committee on hardness; and because NIST is the Secretariat for the International Organization of Legal Metrology (OIML) TC10/SC5 committee on hardness, we are revising the international requirements for regulating hardness.

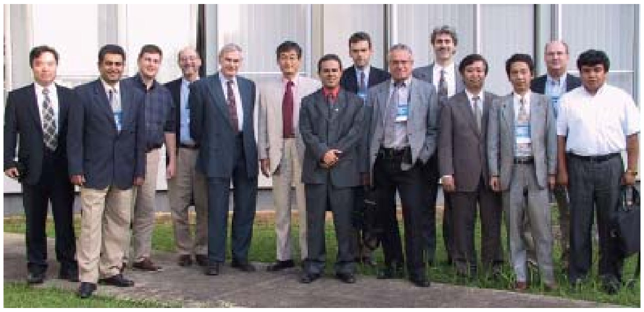


Figure 1: *Attendees of the 5th WGH meeting at INMETRO (Brazil) in May 2002, representing international standards organizations and the hardness laboratories of nine NMIs.*

National Activities

Our primary task at the national level is to standardize the U.S. national hardness scales and to provide a means of transferring these scale values to industry. Currently, we are producing test block Standard Reference Materials® (SRMs) for the Rockwell, Vickers and Knoop hardness scales (Figure 2), as well as developing new reference standards. Ten different microhardness SRMs for Vickers and Knoop hardness are now available. Using electro-deposition technology, the standards are produced with uniform properties and microstructure. Work is progressing in developing a prototype high hardness Vickers microhardness SRM having a hardness range of 750 to 800.

Figure 2: *SRM test blocks for Rockwell, Vickers and Knoop hardness (metals).*

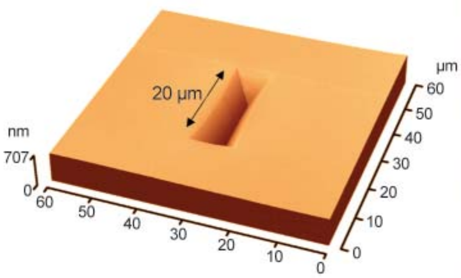
We also completed the calibration of three new SRMs for the Rockwell B scale (HRB) to compliment the three SRM Rockwell C scale blocks currently available. The HRB scale is used for testing softer metals, such as aluminum, copper and brass. Initial work is also being planned to produce a new Rockwell indenter SRM, which has become feasible due to the successful completion of a Small Business Innovative Research (SBIR) Phase-2 project with Gilmore Diamond Tools to develop an improved method for manufacturing geometrically correct Rockwell diamond indenters.

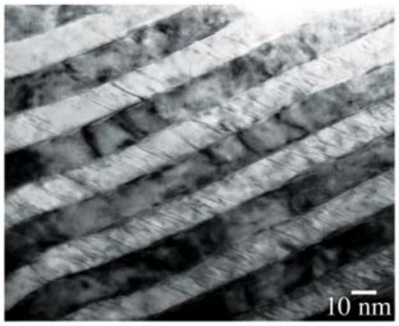
It is important that knowledge gained from the NIST calibration work be shared with industry. Since the new *NIST Recommend Practice Guide: Rockwell Hardness Measurement of Metallic Materials* was published in May 2001, almost 5000 copies have been requested by and distributed to industrial facilities.

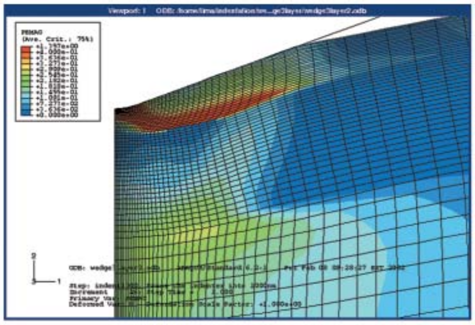
Contributors and Collaborators

J. Song, C. Evans, R. Clary (NIST/MEL); W. Liggett, Jr., N. Zhang (NIST/ITL); C. Beauchamp, D. Faison, W. Stiefel (NIST/TS); M. Mihalec (Gilmore Diamond Tools, East Providence, RI)

Deformation Mechanisms and Constitutive Laws in Thin Film Superlattices







Thin film superlattices exhibit favorable deformation and wear properties compared to existing protective coatings. However, little understanding of the deformation mechanisms or constitutive laws governing deformation in these materials exists, making it difficult to assess lifetime estimates, cost feasibility or perform predictive modeling. This project aims to combine experimental and computational methods to study deformation mechanisms and stress/strain relations in thin film superlattices.

Donald E. Kramer and Timothy J. Foecke

The mechanical properties of thin films can play an important role in the design and reliability of devices. Regardless of the material property of interest, mechanical integrity must be maintained to assure proper device performance. However, measurement and modeling of thin film mechanical properties present significant challenges without knowledge of an appropriate constitutive law for deformation. This is particularly true for thin film superlattices. These thin film materials are composed of hundreds to thousands of alternating layers of two different materials. Each layer may be from single to tens of nanometers in thickness. The result of this layered structure is a material that exhibits high resistance to deformation and wear. The superlattice derives its strength from the high density of bi-material interfaces. However, neither the mechanism by which these interfaces provide that strength nor the quantitative effect on the stress/strain relationship is well understood.

Nanoindentation is an experimental tool that can probe the mechanical properties of surfaces with nanometer depth sensitivity. This makes it a potentially useful tool for studying the mechanical properties of thin films. However, at the nanometer length scale, extraction of mechanical properties is not straightforward due to the discreet nature of the lattice, the influence of substrate mechanical properties, and the large strain gradients under the indenter.

To solve this problem, research was underway in FY2002 to characterize the physical processes and deformation structures that arise during nanoindentation and, using multi-scale modeling and simulation, develop a framework for prescribing stress/strain relationships. A technique to observe the deformation structures with transmission electron microscopy (TEM) under nano-scale contacts was developed last year at NIST. This approach uses a wedge indenter to impose a line of deformation on the surface rather than a single point. An example of the surface deformation can be seen in the atomic force microscopy image on the left. This has two advantages: the deformation zones under these indents can be readily located in the TEM and the plane strain conditions under the wedge reduce the computational intensity for methods such as finite element simulations.

An example of the deformation structure in a W/NbN superlattice is shown in the middle figure as seen by TEM. The superlattice is embedded below a 250 nm layer of tungsten. The direction of indentation is from the top normal to the layer interfaces with the long axis of the wedge normal to the image plane. Planar defects are seen in the lighter NbN layers, while the dark W layers are comparatively defect free.

The finite element simulation in the right figure was compared to the observed deformation field to understand where plastic strain initiated and the volume into which it expanded. The mesh consists of a 1 μm superlattice layer sandwiched between a 250 nm tungsten capping layer and a tungsten substrate. As the indenter compresses the capping layer, plastic deformation in the embedded superlattice initiates at the lower film/substrate interface and expands toward the capping layer interface. These experiments help in the development of deformation mechanisms and, hence, constitutive equations that operate for nanolayers.

Contributors and Collaborators

M.F. Savage, L. Ma, D.T. Smith (NIST); P.M. Anderson (Ohio State University); S.A. Barnett (Northwestern University); H. Kung (Los Alamos National Laboratory)

Analysis of Structural Steel in the World Trade Center Investigation

In 2002, NIST became the lead agency in a planned investigation of the World Trade Center collapse. The investigation addresses many aspects of the catastrophe, from occupant egress to factors affecting how long the Twin Towers stood after being hit by the airplanes, with the goal of gaining valuable information for the future. A critical aspect of the investigation is the metallurgical and mechanical analysis of structural steel from the Twin Towers and WTC 7. The analysis includes characterization of properties, failure modes, and temperature excursions seen by the steel.

Frank W. Gayle, Richard J. Fields,
and Stephen W. Banovic

The collapse of the twin World Trade Center towers on September 11, 2001 was the worst building disaster in human history. Engineers, emergency responders, and the nation did not anticipate, and were largely unprepared for, such a catastrophe. Among other national needs, these events highlight the following technical priorities:

- To establish the probable technical causes of the collapses and derive the lessons to be learned;
- To develop and disseminate immediate guidance and tools to assess and reduce future vulnerabilities; and
- To produce the technical basis upon which cost-effective changes to national practices and standards can be developed.

NIST has prepared a technical investigation plan to address these issues (see <http://wtc.nist.gov/>). A primary objective of the investigation is to determine why and how the World Trade Center Buildings collapsed after the initial impact of the aircraft. To aid in this investigation, more than 100 WTC steel structural elements were brought to NIST to be studied. The NIST Metallurgy and Materials Reliability Divisions' project to study the steel is outlined here.

Task 1 — Identification of steel. Steels in the exterior and core columns, welds, spandrels, trusses, truss seats, and fasteners of the WTC Towers 1 and 2, and WTC 7 will be identified based on composition, microstructure, and mechanical properties, and compared to specifications from the period.

Task 2 — Failure mechanisms based on visual evidence. Steel pieces at NIST, and evidence available from other sources, will be examined and documented as to failure mechanisms.

Task 3 — Property data to support structure performance and airplane impact modeling studies. In addition to the mechanical properties provided in Task 1, the steels in the exterior and core columns, welds, spandrels, and fasteners of WTC 1 and 2 will be tested for high strain rate properties, including tensile and yield strength, ductility, and impact properties.

Task 4 — Steel property data to support models of steel frame performance in fire. Creep and high temperature tensile properties will be measured for columns, bolts on columns, trusses, hangers, and bolts or welds associated with truss seats.

Task 5 — Steel property data to support models of steel performance during collapse. High-strain-rate, room-temperature tensile properties will be measured for truss seats and associated bolts and welds.

Task 6 — Models of elevated temperature deformation behavior. Models of elevated temperature deformation as a function of load and time at temperature will be provided for relevant steels, giving deformation information for steels with any given history of loading and temperature.

Task 7 — Determination of maximum temperatures exposure. The steel will also be analyzed to estimate maximum temperatures reached, although it is recognized that high temperature exposure before the collapse may be difficult or impossible to distinguish from exposure during post-collapse fires. Studies of paint condition on the steel, microstructural changes in the steel, and stress relief in high strength bolts, washers, and weld zones will be done.

(Skilling Ward Magnusson Barkshire Inc.)

Figure 1: *Exterior columns and floor trusses during WTC tower construction. These critical elements of the steel structure will be characterized in the NIST investigation.*

Contributors and Collaborators

J.D. McColskey, T. Siewert, C. McCowan, R. Santoyo (Materials Reliability Division, MSEL); T. Foecke, M. Williams, D. Kelley, S. Claggett, W. Luecke, J. Cahn (Metallurgy Division, NIST Materials Science and Engineering Laboratory); P. Brand (NIST Center for Neutron Research, MSEL); John Gross (NIST Building and Fire Research Laboratory)

Materials Structure Characterization

Materials science and engineering is the area of science concerned with understanding relationships between the composition, structure, and properties of materials and the application of this knowledge to the design and fabrication of products with a desired set of properties. Thus, measurement methods for the characterization of materials structure are a cornerstone of this field. MSEL supports a wide array of techniques and instrumentation for materials measurements. Facilities include optical and electron microscopy, optical and electron scattering and diffraction, and major x-ray facilities at the National Synchrotron Light Source (NSLS) at Brookhaven Laboratory, and at the Advanced Photon Source (APS) at Argonne National Laboratory.

Synchrotron radiation sources provide intense beams of x-rays enabling leading-edge research in a broad range of scientific disciplines. Materials characterization using x-rays from synchrotron sources forms a major part of the Materials Structure Characterization Program. This includes the development and operation of experimental stations at the NSLS and at the APS. At the NSLS, NIST operates a soft x-ray station in partnership with Dow and Brookhaven National Laboratory. At the APS, NIST is a partner with the University of Illinois at Urbana/Champaign, Oak Ridge National Laboratory, and UOP, in a collaboration called UNICAT. At both facilities, NIST scientists, and researchers from industry, universities, and government laboratories, perform state-of-the-art measurements on a wide range of advanced materials. Studies currently underway include: ceramic coatings; defect structures arising during deformation of metals, ceramics, and polymers; defect structures in semiconductors and single-crystal proteins; and atomic-scale and molecular-scale structures at surfaces and interfaces in polymeric, catalytic, and metal/semiconductor systems.

Ceramic powders are precursors for over 80% of ceramic manufacturing. As a result, a major focus in the Ceramics Division is the accurate and reliable measurement of the physical and chemical properties of ceramic powders, including sub-micrometer and nanometer sized powders. These measurements are critical to ensuring processes and products of high quality, minimal defects, and consequent economic benefits. Another area of concern to ceramic manufacturing is powder dispersion in a fluid vehicle for shape forming and other uses. The chemical and physical characteristics of powders dispersed in liquids are evaluated to understand the influence of surface charge, dissolution, precipitation, adsorption, and other physicochemical processes on the dispersion behavior. In addition to these activities, standard reference materials for use as primary calibration standards and national/international standards for particle size and size distribution, pore volume, and particle dispersion measurements are being developed in collaboration with industrial partners, measurement laboratories, and academic institutions in the U.S., Europe, and Asia.

The NIST effort in materials characterization has a strong emphasis on electron microscopy, which is capable of revealing microstructures within modern nanoscale materials and atomic-resolution imaging and compositional mapping of complex crystal phases with novel electronic properties. The MSEL microscopy facility consists of two high-resolution transmission electron microscopes (TEM) and a high-resolution, field-emission scanning electron microscope (FE-SEM) capable of resolving features down to 1.5 nm. Novel experimental techniques using these instruments have been developed to study multilayer and nanometer-scale materials.

Through this MSEL Program, measurement methods, data, and standard reference materials (SRMs) needed by the U.S. polymers industry, research laboratories, and other federal agencies are provided to characterize the rheological and mechanical properties of polymers and to improve polymer processibility. In response to critical industry needs for *in-situ* measurement methodologies, a substantial effort is underway to develop optical, dielectric, and ultrasonic probes for characterizing polymer processing. Improved methods for determining molecular mass distribution of polymers are developed because of the dramatic effect it has on processibility and properties. Mechanical properties and performance are significantly affected by the solid-state structure formed during processing. Importantly, unlike many other common engineering materials, polymers exhibit mechanical properties with time dependent viscoelastic behaviors. As a result, techniques are being developed that measure the solid-state structure and rheological behavior of polymeric materials. Recent program activities exploit advances in mass spectrometry using matrix assisted laser desorption ionization (MALDI) to develop a primary tool for the determination of the molecular masses of synthetic polymers, with particular emphasis on commercially important polyolefins. The polymer industry and standards organizations assist in the identification of current needs for SRMs, and based on these needs, research on characterization methods and measurements is conducted leading to the certification of SRMs.

Contact: John E. Bonevich

Nanoscale Characterization: Electron Microscopy

Electron microscopy is used to characterize the structure and chemistry of materials at the nanometer scale to better understand and improve their properties. New measurement techniques in electron microscopy are being developed and applied to materials science research. The MSEL Electron Microscopy Facility primarily serves the Metallurgy, Ceramics, and Polymers Divisions as well as other NIST staff and outside collaborative research efforts.

John E. Bonevich

Atomic-scale structure and compositional characterization of materials can lend crucial insights to the control of their properties. For instance, direct observation of local structures by transmission electron microscopy (TEM) provides an important information feedback to the optimization of crystal growth and processing techniques. Various characteristics may be observed such as crystal structure and orientation, grain size and morphology, defects, stacking faults, twins and grain boundaries, second phase particles — their structure, composition and internal defect structure, compositional variations and the atomic structure of surfaces and interfaces.

The MSEL Electron Microscopy Facility consists of two transmission electron microscopes, three scanning electron microscopes, a specimen preparation laboratory, and an image analysis/computational laboratory. The JEOL3010 UHR-TEM has atomic scale resolution as well as detectors for analytical characterization of thin foil specimens. An X-ray detector (EDS) provides compositional analysis and an energy-selecting imaging filter (IF) allows compositional mapping at atomic resolution. The JSM6400 is equipped with electron backscattered diffraction/phase identification (EBSD) and EDS systems for characterization of texture and composition of materials.

FY2002 Highlights

- ATP intramural research collaboration with the Semiconductor Electronics and Electricity Divisions (EEEL) to characterize quantum effects in confined Si devices.
- ATP intramural research collaboration with the Optoelectronics Division (EEEL) to characterize quantum dot III-V materials.
- Measurement of size distributions in CeO_2 nanoparticles for use as an x-ray particle size standard reference material.
- Characterization of superconformal deposition of silver in sub-100 nm features for on-chip interconnections.

The shape of self-assembled quantum dots (QDs) play a major role in their electronic properties. In conjunction with RHEED and AFM, TEM studies of QD shape and faceting have revealed novel structures in $In_{0.44}Ga_{0.56}As$ (see Figure 1). Typical models for QD shape include hexagonal dots as well as diamond shaped pyramids. However, TEM results show unusual facets. Instead of appearing with trapezoidal or triangular cross-sections, the QDs have multiple facets at their peaks and bases. The varied shapes have implications for the control and reproducibility of the MBE growth process of QDs.

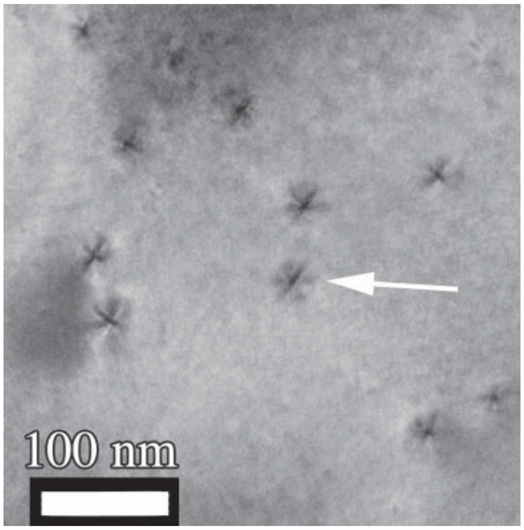


Figure 1: *Plan-view TEM of InGaAs QDs reveals "X" features indicating the shape due to surface facets. Some QDs have additional facets (arrowed).*

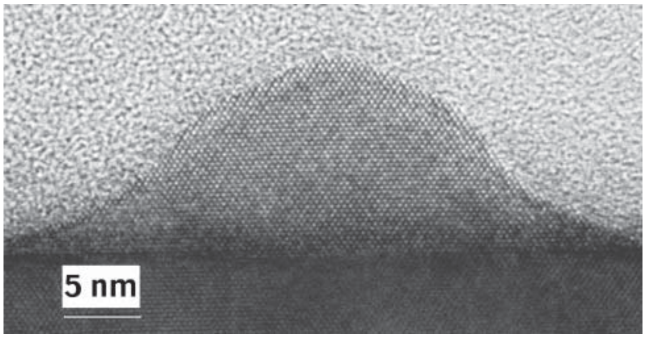


Figure 2: *Cross-sectional HRTEM of InGaAs QDs indicating unusual faceting.*

Contributors and Collaborators

R.D. McMichael, D. Josell, T.P. Moffat, J. Cline (MSEL); A. Roshko, S. Lehman (EEEL); E. Vogel, N. Zimmerman (EEEL); Prof. A. Stanishevsky (University of Maryland, Institute for Plasma Research)

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Metallurgy Division

Chief

Carol A. Handwerker
Phone: 301–975–6158
E-mail: carol.handwerker@nist.gov

Deputy Chief

Frank W. Gayle
Phone: 301–975–6161
E-mail: frank.gayle@nist.gov

NIST Fellows

William J. Boettinger
Phone: 301–975–6160
E-mail: william.boettinger@nist.gov

John W. Cahn
Phone: 301–975–5664
E-mail: john.cahn@nist.gov

Group Leaders

Electrochemical Processing Group

Gery R. Stafford
Phone: 301–975–6412
E-mail: gery.stafford@nist.gov

Magnetic Materials Group

Robert D. Shull
Phone: 301–975–6035
E-mail: robert.shull@nist.gov

Materials Performance Group

Stephen D. Ridder
Phone: 301–975–6175
E-mail: stephen.ridder@nist.gov

Materials Structure and Characterization Group

Frank W. Gayle
Phone: 301–975–6161
E-mail: frank.gayle@nist.gov

Metallurgical Processing Group

Stephen D. Ridder
Phone: 301–975–6175
E-mail: stephen.ridder@nist.gov

Research Staff

Banovic, Stephen W.
E-mail: stephen.banovic@nist.gov
Metal forming
Mechanical properties
Texture analysis

Beauchamp, Carlos R.
E-mail: carlos.beauchamp@nist.gov
Compositionally modulated alloys
Standard reference materials

Baker, Brett C.
E-mail: brett.baker@nist.gov
Deposition of metals/alloys

Bendersky, Leonid A.
E-mail: leonid.bendersky@nist.gov
Functional ceramics
Analytical and high-resolution TEM
High-temperature intermetallics
Combinatorial methods

Biancaniello, Frank S.
E-mail: frank.biancaniello@nist.gov
Spray deposition measurements and diagnostics
Inert gas atomization: metal powder measurements and consolidation
Nitrogenated steels, standard reference materials
Special alloys, bulk metallic glasses
Biomaterials

Boettinger, William J.
E-mail: william.boettinger@nist.gov
Relation of alloy microstructures to processing conditions; solidification
Thermal analysis
Solder

Bonevich, John E.
E-mail: john.bonevich@nist.gov
Electron holography
Interfacial structure and chemistry
High resolution/analytical electron microscopy
Magnetic materials

Boyer, Paul A.
E-mail: paul.boyer@nist.gov
Powder analysis
Data management
Vacuum technology
Plasma spray

Campbell, Carelyn E.
E-mail: carelyn.campbell@nist.gov
Transient liquid phase bonding
Multicomponent diffusions simulations
Alloy design methodology

Claggett, Sandra W.
E-mail: sandra.claggett@nist.gov
Specimen preparation for electron microscopy
Digital imaging
Specimen preparation for scanning electron microscopy
Image analysis
Metallography of materials
Specimen preparation for transmission of electron microscopy

Drew, Rosetta V.
E-mail: rosetta.drew@nist.gov
Magnetometry
Database maintenance

Egelhoff Jr., William F.
E-mail: william.egelhoff@nist.gov
Giant magnetoresistance
Molecular beam epitaxy
Surface physics
Ultrahigh density data storage

Fields, Richard J.
E-mail: richard fields@nist.gov
Mechanical properties
Mechanical testing
Powder consolidation
Metal forming

Fink, James L.
E-mail: james fink@nist.gov
Hardness standards
Hardness testing
Mechanical properties measurement
Metal powder consolidation
Environmental corrosion
Metallography

Foecke, Timothy J.
E-mail: timothy.foecke@nist.gov
Metal forming standards
Nanostructured materials
Experimental fracture physics
SEM, TEM, SPM
Micro- and nano-mechanics of materials
Dislocation-based deformation mechanisms
Historical metallurgy and failure analysis

Fry, Richard A.
E-mail: richard. fry@nist.gov
SQUID magnetometry
Ferromagnetic resonance
Magnetic dendrimer nanocomposites
Giant magnetoresistance

Gates, Hilary G.
E-mail: hilary.gates@nist.gov
Standard reference materials

Gayle, Frank W.
E-mail: frank.gayle@nist.gov
Structure/property relationships
Transmission electron microscopy
Aluminum metallurgy
Solder science

Guyer, Jonathan E.
E-mail: jonathan.guyer@nist.gov
III-V semiconductors
Molecular beam epitaxy
Alloy film deposition
Stress-induced mass transport

Handwerker, Carol A.
E-mail: carol.handwerker@nist.gov
Interface thermodynamics and kinetics
Solder science
Microstructure evolution

Jiggetts, Rodney D.
E-mail: rodney.jiggetts@nist.gov
Substrate analysis
Grit blasting
Roughness measurements
Metallography of coatings
Image analysis
Micro analysis/characterization
Hot isostatic processing

Johnson, Christian E.
E-mail: christian.johnson@nist.gov
Ultra-black coatings
Electroless deposition processes
Metallic glass alloy deposition
Microhardness SRM research
Chromium deposition
Pulse alloy deposition
Lead-free solder

Josell, Daniel
E-mail: daniel.josell@nist.gov
Mechanical and thermal properties of multilayer materials
Measurement and modeling of solder joint geometries
Filling of sub-0.1mm features by electrodeposition

Kattner, Ursula R.
E-mail: ursula.kattner@nist.gov
Computational thermodynamics
Alloy phase equilibria evaluations
Solder alloy systems
Superalloy systems

Kelley, David R.
E-mail: david.kelley@nist.gov
Microhardness SRM development
Dye penetrant SRM development
Precious metal electrodeposition
Plating on aluminum
Electroplating

Kramer, Donald E.
E-mail: donald.kramer@nist.gov
Nanoindentation
Atomic force microscopy
Thin film mechanical behavior
Transmission electron microscopy
Nanostructured material

Kunz, Andrew W.
E-mail: akunz@nist.gov
Micromagnetic calculations

Levine, Lyle E.
E-mail: lyle.levine@nist.gov
Diffraction theory
Dislocation-based deformation
Synchrotron x-ray techniques
Percolation theory
TEM, SEM, SPM

Lewis, Daniel J.
E-mail: daniel.lewis@nist.gov
Modeling of eutectic solidification
Electric packaging

Lobkovsky, Alexander E.
E-mail: alexander.lobkovsky@nist.gov
Formation and evolution of microstructure
Plasticity
Dynamics of crystalline defects
Thermodynamics of fluid membranes

Low II, Samuel R.
E-mail: samuel.low@nist.gov
Hardness standards
Hardness testing
Mechanical properties of materials
Mechanical testing of materials

Mates, Steven P.
E-mail: steven.mates@nist.gov
Compressible fluid flow
Metal sprays
Fluid flow visualization

McMichael, Robert D.
E-mail: robert mcmichael@nist.gov
Giant magnetoresistance
Micromagnetic modeling
Ferromagnetic resonance
Nanocomposites

Moffat, Thomas P.
E-mail: thomas.moffat@nist.gov
Electrochemistry
Scanning probe microscopy
Nanostructures

Pierce Jr., Thomas A.
E-mail: tpierce@nist.gov
Hardness measurements
Metallography

Pitchure, David J.
E-mail: david.pitchure@nist.gov
Mechanical testing
Computer-aided design
Mechanical engineering

Ricker, Richard E.
E-mail: richard.ricker@nist.gov
Corrosion
Deformation mechanisms
Fracture mechanisms (SCC, CF HE)
TEM, SEM

Ridder, Stephen D.
E-mail: stephen.ridder@nist.gov
Spray dynamics and deposition
Thermal spray processes
Process modeling and control

Savage, Michael F.
E-mail: michael.savage@nist.gov
Mechanical behavior
Dislocation deformation mechanisms
Transmisssion electron microscopy
Titanium alloys and intermetallics

Shapiro, Alexander J.
E-mail: alexander.shapiro@nist.gov
MOIF method microscopy
Mössbauer effect
Scanning electron microscopy (SEM) and X-ray microanalysis
Image analysis

Shepherd, Dominique, A.
E-mail: dominique.shepherd@nist.gov
Titanium alloys
Mechanical testing
Mechanical properties
SEM, TEM

Shull, Robert D.
E-mail: robert shull@nist.gov
Nanocomposites
Magnetic susceptibility
Mössbauer effect
X-ray and neutron diffraction
Magneto-caloric and magneto-optical effects
Magnetic domain imaging

Siu, I-Liang
E-mail: iliang.siu@nist.gov
Thin film processing
Giant magnetoresistance
Magnetization dynamics

Slutsker, Julia
E-mail: julia.slutsker@nist.gov
Smart composites
Shape memory alloy
Massive transformations
Superelastic material

Stafford, Gery R.
E-mail: gery.stafford@nist.gov
Electrochemical transients
Electrodeposition
Molten salt electrochemistry

Stoudt, Mark R.
E-mail: mark.stoudt@nist.gov
Metal fatigue
Thin films
Mechanical properties
Environmentally assisted cracking

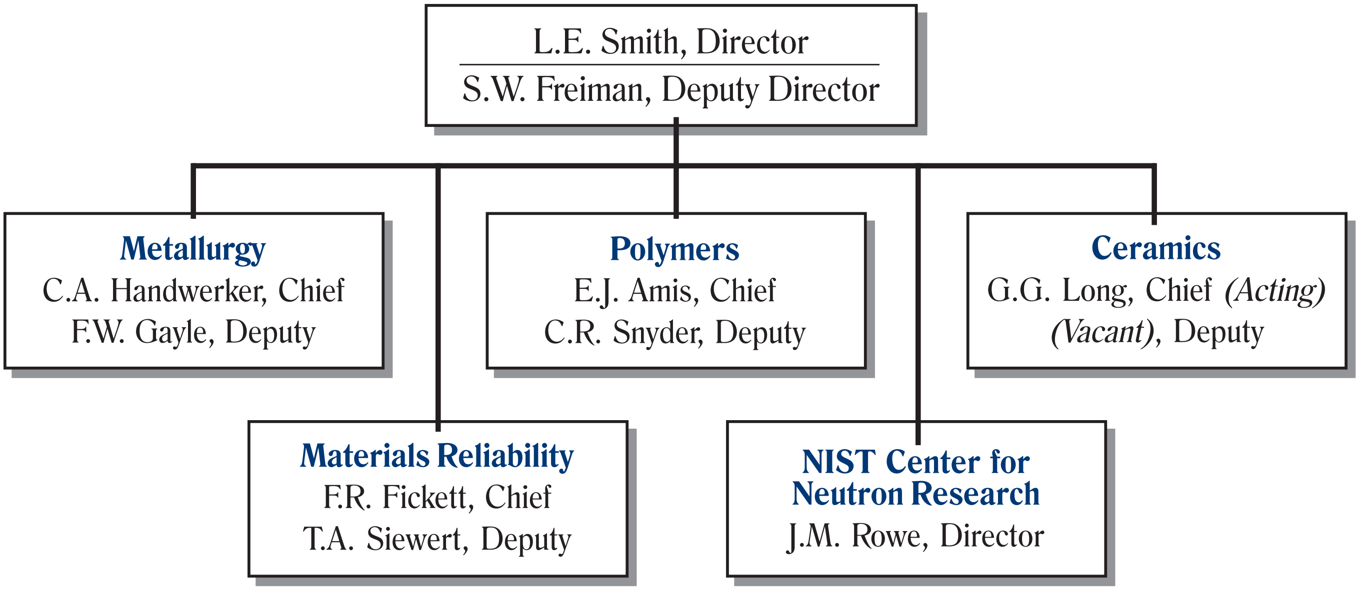
Twisselmann, Douglas J.
E-mail: douglas.twisselmann@nist.gov
Ferromagnetic resonance
Magnetometry

Warren, James A.
E-mail: james.warren@nist.gov
Computer simulations of solidification
Dendrite pattern formation
Modeling of solder/substrate wetting processes
Modeling grain boundaries

Williams, Maureen E.
E-mail: maureen.williams@nist.gov
Differential thermal analysis
Powder x-ray diffraction
Solder wettability
SEM

Organizational Charts

Materials Science and Engineering Laboratory



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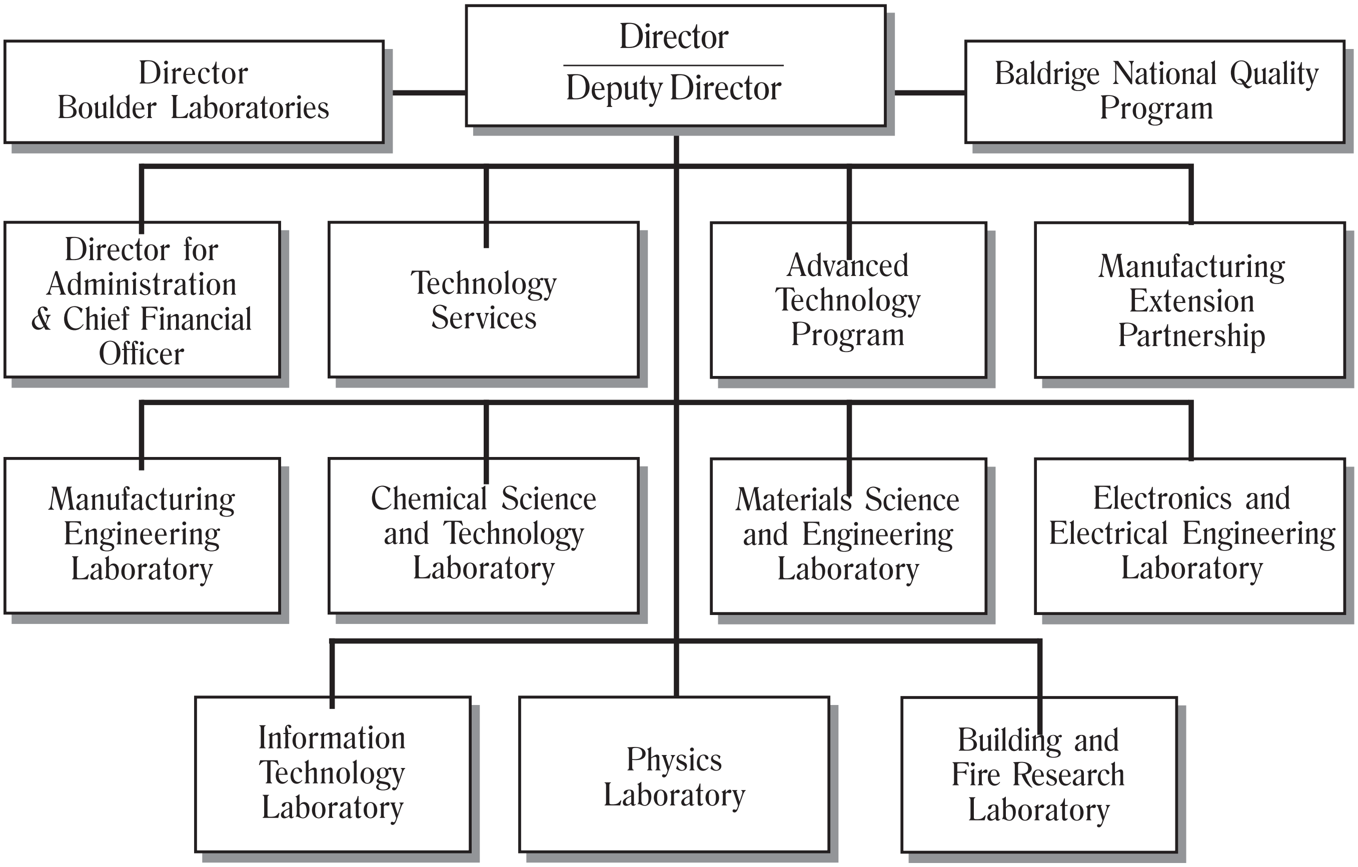

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