Laboratory Name: Sandia National Labs/NM
B&R Code: KC020101

FWP and possible subtask under FWP:
Physics and Chemistry of Ceramics

FWP Number: SCW 1953

Program Scope:
To develop an understanding of how chemical and physical processes determine structure and structural evolution in inorganic materials and to provide insight about how to control and direct structure development at specific scales and to enable the creation of structural hierarchy across multiple length scales. The work focuses on self-assembly of mesoporous materials, complex mixed-metal alkoxides precursors for the synthesis of nanoparticles and films, the physics of structure and flow of granular ceramics, and new characterization techniques for studying structure and bonding using Nuclear Magnetic Resonance (NMR) spectroscopy.

Major Program Achievements (over duration of support):
Developed numerous novel methods for synthesizing highly porous ceramics and self-assembling inorganic-based materials with tightly controlled microstructures. Discovery of a method for functionalizing bonds in silica aerogels so that extremely porous ceramics could be made at ambient temperature and pressure was a major achievement in this field. Recent breakthroughs in methods to make films and particles with various types of structured porosity are leading the understanding of evaporation-induced self-assembly.

Developed methods for synthesizing a broad family of novel metal and mixed-metal inorganic precursors for films and nanoparticles based on our understanding of alkoxide chemistry. Correlated the topology and chemistry of the precursors, based on single crystal diffraction and solid-state NMR techniques, to the resulting ceramic material.

Developed a highly-parallel, molecular dynamics code to simulate properties of granular compacts with millions of particles, which is necessary to evaluate critical physics. Simulations have shown how coordination number in granular materials depends on friction coefficients and has given insight to flow properties and stress buildup.

Program Impact: Over many years, this program has provided key insights as to how various aspects of solution chemistry and physical interactions determine the structure and chemistry of inorganic solids. This work has impacted the understanding of materials with nanostructured porosity, thin films, glasses and granular compacts.

Interactions:
F. Babonneau (Chimie de la Matiere Condensee, Universite Paris), D. Bonnel (University of Pennsylvania), R. Brow (University of Missouri – Rolla), B. Dunn (UCLA), A. Gibaud (l'Universite du Maine), T. Halsey (Exxon Mobil R&E), J. U. Otaigbe (Iowa State University), D. Payne (University of New Mexico), B. Scott (Los Alamos Naltional Lab), T. Ward (University of New Mexico), J. Ziller (University of California – Irvine), J. Zink (UCLA), Y. Lu (Tulane Univ.), V. Colvin (Rice Univ.), O. Auciello (Argonne National Lab).

Recognitions, Honors and Awards (at least in some part attributable to support under this program):
C.J. Brinker – Inducted into National Academy of Engineers – Elected February 2002.
C.J. Brinker – E.O. Lawrence Award, U.S. Department of Energy, October 2002.
T.J. Boyle – John Dustin Clark Award (Am. Chem. Soc.) for outstanding contribution to chemistry in New Mexico.
D. Doshi – MRS Gold Medal (2002).
C.J. Brinker – Fellow of the American Ceramic Society.
T.J. Boyle – Motorola Award for outstanding mentoring of students.

Personnel Commitments for FY2002 to Nearest +/- 10%:
Todd Alam (25%), Timothy Boyle (30%), Jeff Brinker (20%), Gary Grest (35%), Frank van Swol (35%). In addition, six post docs and six students are currently working on this project.

Authorized Budget (BA) for FY00, FY01, FY2002:
FY00 BA $945 K **FY01 BA $920 K** **FY02 BA $895 K**

Laboratory Name: Sandia National Labs/NM
B&R Code: KC020101

FWP and possible subtask under FWP:
Theory of Microstructures and Ensemble Controlled Deformation

FWP Number: SCW 5957

Program Scope:
The goal of this program is to combine experiment, modeling, and simulation to construct, analyze, and evolve polycrystalline microstructures. A genetic algorithm is utilized to build three-dimensional polycrystals in a physically correct manner. The resulting microstructures are input into network analysis models to characterize parameters that influence material properties. Finally, these microstructures provide input for highly realistic microstructural evolution simulations on the grain and subgrain scales. This program is new in FY02 and supports the LANL initiative, "Ensemble-Controlled Deformation Behavior in Materials."

Major Program Achievements (over duration of support):
Delineated the local and global conditions under which abnormal subgrain growth occurs. This analysis provides the foundation for a physically based model for abnormal grain and subgrain growth, as well as the first self-consistent structural model for nucleation of recrystallized grains.

Devised a strategy for constructing three-dimensional (3D) microstructures from two-dimensional (2D) data. A genetic algorithm that evolves cellular automaton algorithms to construct 3D microstructures from 2D metallographic data using correlation functions as fitness selectors was developed and successfully tested on model microstructures.

Compared the physics and results of atomistic, phase-field, and spin models for microstructural development, providing the most rigorous comparison between these commonly utilized approaches to date.

Program impact:
This program is targeted toward understanding microstructural evolution and the resulting material properties in polycrystals with the most realistic structure, crystallography, and boundary properties yet studied. The results of this effort will enable optimization of materials design and processing, as well as predictive models of materials performance.

Interactions:
Los Alamos National Laboratory (R. A. LeSar, M. Baskes, et al.)
King's College London (Prof. M. A. Miodownik)
Colorado School of Mines (Prof. M. A. Lusk, Prof. M. Upmanyu)
Timken Corporation/DOE Office of Industrial Technology
Purdue University (Prof. A. H. King)
Michigan State University (Prof. P. Duxbury)
Princeton University (Prof. D. J. Srolovitz)

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Fellow of ASM International (2002) to E. A. Holm
Distinguished Member of Technical Staff (2002) to E. A. Holm
Nuffield Foundation Grant (2002) to M. A. Miodownik to support collaboration on this work
Four invited presentations in first year of project (FY02)

Personnel Commitments for FY2002 to Nearest +/- 10%:
Elizabeth A. Holm (principal investigator) 30%
Stephen Foiles (staff member) 10%
Joseph Arellano (technician) 25%
Prof. Mark Miodownik and student, King's College London, $50k contract

Authorized Budget (BA) for FY00, FY01, FY02:

FY00 BA $ **FY01 BA $** **FY02 BA $170 K**

Note: Elements of these projects were a part of the Physics and Chemistry of Ceramics project prior to FY02.

Laboratory Name: Sandia National Labs/NM

B&R Code: KC020102

FWP and possible subtask under FWP:
Atomic Level Science of Adhesion and Interfacial Wetting

FWP Number: SCW 2443

Program Scope: The development of an atomistic understanding of the chemical and physical interactions that control solid/solid and solid/liquid interface formation, thereby enabling us to: (1) develop predictive models for adhesive bond strength, interfacial stability, and flow kinetics; and (2) tailor material surfaces for optimized adhesion, wetting or lubrication.

Major Program Achievements (over duration of support):
IFM Invention: We invented the world's first (and only) scanning probe instrument that can simultaneously measure normal and lateral forces throughout the entire attractive/repulsive interaction regime with atomic-level sensitivity. This has revolutionized fundamental research in nanomechanics, adhesion, friction and tribology.

Nanomechanics: Nanoscale deformation experiments coupled with atomistic simulation have led to the understanding of two-stage plasticity in Nanoscale contacts, yield strength softening by surface defects, and interphase mechanical properties in nanocomposite materials.

Monolayer Tribology: IFM and acoustic wave damping studies have identified distinct physical and chemical contributions to friction for self-assembled alkanethiol monolayers in dynamic contact, structure-dependent mechanisms of energy dissipation, and environmental degradation processes.

Interfacial Fluids: Both theory and experiment are revealing surprises in how liquids behave at solid surfaces. Nanometer thick interfacial fluids exhibit almost solid-like viscoelastic properties, and even the structure of a water layer on a metal surface isn't a simple as once presumed.

Program Impact:
The new approaches and techniques developed in this project are finding broad application in the international research community; e.g., the IFM is use in 17 laboratories. By combining advanced experimental techniques (IFM, LEEM, AWD) with first-principles theory and simulation, technologically important interfacial phenomena are becoming better understood scientifically.

Interactions:
Princeton University, Air Force Research Lab, University of Houston, Drexel University, University of Minnesota, South Dakota School, University of Texas at Austin, Goodyear Corporation.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

Publications in *Science*, *Nature*, *Physics Today*, *MRS Bulletin*, *Physical Review Letters*
15 Invited talks since 2001
Fellows of the AVS and APS (Swartzentruber, Houston, Kellogg, Bartelt)
Conference Chairs, Symposia Organizers (Kellogg, Shinn)
Materials Research Society Medal (2001, Bartelt)
Professional society officers -- AVS, IUVSTA (Shinn, Kellogg)
Associate Editor of PRL (Feibelman) and JVST (Shinn)

Personnel Commitments for FY2002 to Nearest +/-10%:
J. E. Houston (staff) 40%, G. L. Kellogg (staff) 20%, P. J. Feibelman (staff) 20%, W. L. Smith (staff) 40%, A. Oliver (post-doc) 100%, N. Simmons (technologist) 40%, N. Bartelt (staff) 10%, E. Webb (staff) 10%, N. D. Shinn (manager) 10%

Authorized Budget (BA) for FY00, FY01, FY02:
FY00 BA $699 K **FY01 BA $643 K** **FY02 BA $635 K**

Laboratory Name: Sandia National Labs/NM
B&R Code: KC020103

FWP and possible subtask under FWP:
Field-Structured Anisotropic Composites and Complex Cooperative Phenomena in Disordered Ferroelectrics and Dielectrics. Subtask on Complex and Cooperative Phenomena….

FWP Number: SCW 1057

Program Scope:
The objective of this task is to understand the properties of ferroelectrics and relaxors and the mechanism for ferroelectric-to-relaxor crossover in compositionally-disordered ferroelectrics. One aspect of this work is the behavior of such systems in the quantum regime and at the displacive quantum limit. This is the limit where $T_c \rightarrow 0$ K and quantum fluctuations come into play, qualitatively changing the nature of the response. The conventional approach for studying these phenomena is to introduce disorder or to shift T_c close to 0 K by chemical substitution. However, this approach introduces compositional fluctuations, clustering, lattice strains and changed interactions, which complicate physical interpretation. Our approach emphasizes the use of high pressure. By compressing the lattice we only change the balance between long-range and short-range interactions making it easier to get to the essential physics.

Major Program Achievements (over duration of support):
- Discovered a pressure-induced ferroelectric (FE)-to-relaxor (R) crossover in compositionally-disordered ABO_3 type ferroelectrics and demonstrated that this phenomenon is a general feature of soft mode ferroelectrics with random site dipolar impurities, or polar nanodomains, unambiguously showing that the relaxor state is the ground state at high pressure (or reduced volume). The physical mechanism for the crossover was understood in terms of soft mode theory, and the main features of the results are in accord with predictions from model Hamiltonians
- By shifting the ferroelectric or glass transition temperature to near 0 K by the application of pressure, we have revealed the manifestations of quantum fluctuations on ferroelectric and relaxor properties including suppression of T_c and the eventual formation of a quantum paraelectric state. Because the characteristic energies are small in the quantum regime, both pressure and biasing electric fields were shown to have strong influences on the properties in this regime.

Program impact:
Relaxor behavior has been the recent hot topic in ferroelectricity. This work has identified the mechanism for ferroelectric-to-relaxor crossover in ABO_3 perovskite ferroelectrics. The work is also making it possible to study and understand the manifestations of quantum fluctuations on the properties of ferroelectrics by avoiding the complications of changing many of the relevant interactions by chemical substitution. Pressure is a much "cleaner" variable.

Interactions:
This work is of much interest to, and interacts with DOE Defense Programs. The project also interacts with the Oak Ridge National Laboratory (Lynn Boatner), Montana State University (Prof. V. H. Schmidt), the University of Ljubljana (Prof. Robert Blinc), the Tokyo Institute of Technology (Dr. M. Itoh) and Gerhard Mercator University-Duisburg (Prof. W. Kleemann).

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
- A major review, "Ferroelectricity Revisited: Advances in Materials and Physics" appeared in Vol. 56, Solid State Physics, Academic Press (2001).
- 2 invited papers (APS, MRS) in 2002; 1 invited Conference paper in 2001.
- Editorial Board of *Ferroelectrics*.
- Organizing Committee of "Fundamental Physics of Ferroelectrics 2003" Conference.

Personnel Commitments for FY2002 to Nearest +/- 10%:
G. A. Samara (20); E. L. Venturini (30); Postdoc (in '03).

Authorized Budget (BA) for FY00, FY01, FY02:

FY00 BA $50 K **FY01 BA $50 K** **FY02 BA $170 K**

Laboratory Name: Sandia National Labs/NM
B&R Code: KC020103

FWP and possible subtask under FWP:
Field-Structured Anisotropic Composites

FWP Number: SCW 1057

Program Scope: To create and understand the properties of Field-Structured Composites. These novel ceramic/polymer and metal/polymer composites are synthesized by polymerizing a resin around particles having an electric permittivity or magnetic permeability mismatch, while subjecting the suspension to applied electric or magnetic fields. These fields can be applied along as many as three axes simultaneously, and the frequencies and relative phases of ac field components can be selected to create a variety of composites having 1-, 2-, and 3-d particle structures. These composites have greatly enhanced magnetic, dielectric, and transport properties, and the anisotropy of these properties can be tailored over a wide range.

Major Program Achievements (over duration of support):

- Development of new and unexpected methods of controlling composite structures with triaxial magnetic fields, using techniques such as amplitude modulation and two- and three-dimensional heterodyning to produce porous particle foams with greatly enhanced properties along all axes (patent application).
- Developed a self-consistent Brownian Dynamics code called TRIAX to predict the evolution of composite structures in triaxial magnetic and electric fields of arbitrary complexity. TRIAX is successful in predicting the remarkable composite structures that evolve from heterodyning fields applied during the viscosity divergence that accompanies gelation.
- Demonstrated that it is possible to enhance the magnetic and dielectric properties of particle composites significantly along all three axes, as much as 7x that expected for random composites.
- Demonstrated that FSCs exhibit giant thermoresistance, piezoresistance, and chemiresistance, with reversible resistance changes of nearly 12 decades measured (patent issued).
- Demonstrated magneto-optical effects such as field induced transmittance and field induced absorption gratings.
- Demonstrated dramatic reversible nonlinear conduction effects, such as current-limiting thermistor behavior at fields as low as 1 V/cm.
- Developed a *Thermal Chain Model* of the effect of strong thermal fluctuations on magnetic particle suspensions subjected to shear flow and magnetic fields, bridging for the first time the fields of magnetorheology and ferrofluids.
- Developed an analytical theory of electro- and magneto-striction in FCSs, showing that large enhancements are expected.
- Developed a computational fluid dynamics code to predict suspension flow in complex magnetic and electric fields.
- Demonstrated the possibility of magnetic storage media with an underlying magnetic watermark (patent issued).

Program Impact: We have shown that FSCs have properties that can be tailored over a wide range, and have conducted research that shows that these materials can impact a wide variety of technologies. The giant thermoresistance, piezoresistance, and chemiresistance effects that we have observed are unprecedented in other materials; the ability to control the magnetic susceptibility and remanence through magnetic field effects has led to the concept of magnetic storage media with secure information permanently embedded; and the development and understanding of triaxial field effects has led to the ability to synthesize much improved composite materials.

Interactions: DOE Center for Synthesis and Processing, Nanomagnetism.

Recognitions, Honors and Awards: Editorial Board of the Journal of Chemical Physics. DOE "Chunky Bullet" award; numerous invited papers.

Personal Commitments for FY 2002: J. E. Martin (30%), E. Venturini (30%), D. Huber (30%)

Authorized Budget (BA) for FY00, FY01, FY02:

FY00 BA $326 K **FY01 BA $270 K** **FY02 BA $285 K**

Laboratory Name: Sandia National Labs/NM

B&R Code: KC020103

FWP and possible subtask under FWP:
Artificially Structured Semiconductors

FWP Number: SCW 1955

Program Scope: Currently, we are investigating the optical, electrical, and mechanical properties of semiconductors interfaced to aqueous biological systems of cells and molecules. High-efficiency, light-emitting semiconductors tailored for biocompatibility have potential as the ideal probe of proteins within living cells to elucidate protein structure and function in their physiological condition with minimal perturbation. Unfortunately, these materials exhibit some incompatibilities with the biochemistry of cells and related biomolecules. To overcome these limitations, we are investigating functionalized semiconductor surfaces to enhance light emission, mitigate semiconductor degradation, and ease flow of biological fluids across semiconductor surfaces. At the same time, we identify novel interfacial transduction mechanisms for probing biosystems in their native state.

Major Program Achievements (over duration of support):

This program holds several distinctions in the world of compound semiconductor research over the duration of support. It is responsible for the seminal development of strained-layer semiconductor quantum wells that have led to the most efficient laser sources, exceeding 59% quantum efficiency. It also seeded the materials research efforts on the monolithic integration of quantum wells with Bragg heterostructures that led to the development of the vertical cavity surface-emitting laser, now in commercial development as the ideal light source for fiber optic communications. Further, it stimulated some of the initial studies on photonic lattice nanostructures. Currently it is pioneering new uses of biocompatible semiconductor materials and structures for probing biological microsytems, and includes the invention of the biocavity laser.

Program Impact: Basic research on artificially structured semiconductors over the duration of support has led to the development of novel light sources, including strained-layer lasers, vertical cavity surface-emtting lasers, and photonic nanostructures. All of these have been commercialized within the United States and constitute an industry with a market size exceeding hundreds of millions of dollars in annual revenues. Royalties stemming from these commercial products are now finding their way back to help support future research efforts in materials-related science.

Interactions:
University of New Mexico School of Medicine
Los Alamos National Lab
Lawrence Livermore National Lab
Cornell University

Recognitions, Honors and Awards (within the last year):
• 2 BES Materials Science Awards; ER100 Award; Top Ten Health Innovation Award
• Basic Research Needs for Countering Terrorism Committee members
• UNM Cancer Research Consortium
• AIP Virtual Journal Selected Paper
• NIH/COBRE Center Advisory Board, NDSU

• 3 invited review articles, 5 invited talks, 6 publications

Personnel Commitments for FY2002 to Nearest +/-10%:
P. L. Gourley (group leader) 80%
Guild Copeland (tech staff) 20%
A. E. McDonald (tech ass't) 80%
Darryl Sasaki's post doc 50%

Authorized Budget (BA) for FY00, FY01, FY02:
FY00 BA $485 K **FY01 BA $445 K** **FY02 BA $475 K**

Laboratory Name: Sandia National Labs/NM

B&R Code: KC020103

FWP and possible subtask under FWP:
Localized Corrosion Initiation at Nanoengineered Defects in Passive Films

FWP Number: SCW 7517

Program Scope: Develop new insight into the mechanisms of localized corrosion initiation in passive metals through an approach based on the novel and unique application of nanofabrication techniques to simulate specific defect types in well-defined locations. Advanced in situ electrochemical, dielectric, local chemical analyses and *ab initio* density functional theory are used to investigate pit initiation in ways that have not been previously possible. Defects are created using UHV thin film deposition, selective area ion implantation, and local electron-stimulated desorption/halide adsorption. Nanoengineered defects are used to study galvanic corrosion and oxide film breakdown mechanisms, study morphological changes at initiation sites prior to pitting, and explore the role of local variations in oxide structure and chemistry on pit initiation with Analytical Electron Microscopy.

Major Program Achievements (over duration of support):
Microelectrode techniques have been developed to allow localized measurements of pitting behavior in aluminum electrodes. The decrease in pitting susceptibility for small area, pure aluminum electrodes, shows that pit initiation is a stochastic process. The introduction of controlled amounts of Cl^- both localized the pitting sites and confirmed the presence of Cl^- in the sample was required for pit initiation in a sulfate solution.

The evolution of local solution chemistry during corrosion of a model aluminum-copper alloy system has been measured in-situ using fluorescence microscopy. The model alloy, containing an array of single copper particles on isolated Al electrodes showed that corrosion evolved at each particle simultaneously, but accelerated attack is typically dominated by a single pit beneath one particle, while the other particles in the system contribute the balancing cathodic current.

Pore formation was found to occur in a wide variety of aluminum oxides prior to the onset of pitting. Pore size (~10 nm) and density correlate to charge passed under polarization while pore distribution occurs equally on grain boundaries and facets. The link between pore formation and pit initiation is currently under investigation.

Program Impact:
Our approach of using engineered defects in controlled oxides to investigate the early stages of pitting has allowed us to address outstanding questions in corrosion science in a clean, controlled and comprehensive manner. Our results are being incorporated into the framework of models for aluminum corrosion and our approach has influenced the experimental design used by other groups within the corrosion community (e.g., ASU).

Interactions:
Ohio State University: Materials Science and Engineering (Prof. R. Buchheit)

North Carolina State University: Materials Science and Engineering (Prof. J. Hren)
Brookhaven National Laboratories: Energy Sciences and Technology (Dr. H. Isaacs)
University of Virginia: Materials Science and Engineering (Prof. R. G. Kelly)
University of Utah: Chemistry (Prof. H. S. White)

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
17 Invited talks since 2001
2002- H.H. Uhlig Educator's Award, NACE International, and 2002- Lumley Research Award, College of Engineering, OSU, Prof. R. Buchheit

Personnel Commitments for FY2002 to Nearest +/-10%:

N. Missert (technical coordinator) 50%	F. D. Wall 40%	K. R. Zavadil 40%
J. P. Sullivan 35%	D. R. Jennison 15%	J. C. Barbour 10%
C. M. Johnson (post-doc) 80%	D. Elswick (student NCSU) 100%	Y. Kim (student OSU) 100%

Authorized Budget (BA) for FY00, FY01, FY02:
FY00 BA $688 K **FY01 BA $670 K** **FY02 BA $618 K**

Laboratory Name: Sandia National Labs/NM
B&R Code: KC020105

FWP and possible subtask under FWP:
Long Range Particle Interactions and Collective Phenomena in Plasma Crystals

FWP Number: SCW 18850

Program Scope: The goal of this project is to understand the fundamental interaction mechanisms and collective behavior of dust particles suspended in charge neutral plasmas. In nature, dusty plasmas can be found in systems as diverse as microelectronics processing to interstellar regions. Dust profoundly influences the properties of such plasmas and leads to a number of long-range interactions and collective behavior between the micron sized particles. In some cases, the dust particles can form stable, multidimensional arrangements, a plasma dust crystal. We are using a number of established and new diagnostic tools to characterize the particle interactions and are incorporating this understanding into models. Experimental observations are coupled with advanced simulations of macroion systems to enable a direct determination of the nature of macroion interactions and crystal properties.

Major Program Achievements (over duration of support):
First measurements of the ion wakefield induced attractive interaction in 3D crystal structures. Developed a new analysis technique to directly determine the particle-particle interactions potential in 2D plasma dust crystals. Demonstrated the use of curved electrode structures to modify the plasma potential structure. Significantly reduced the upper bound on the strength of in-plane attractive forces in 2D crystalline arrangements. Determined the spatial profile of the time-average electric field responsible for levitating the 2D plasma crystals. Observed significant inter-layer particle interactions in multi-layer, 3D plasma crystals. Developed molecular dynamics simulations to investigate crystal stability phase space. Developed new image processing algorithms for video analysis. Developed new laser techniques to spectroscopicaly determine the sheath electric field

Program impact:
Provided insights into the long range and collective interactions between micro sized dust particles. Our development and use of shaped electrodes to obtain quantitative measurements of the interaction potentials is being used by other research groups. Our electric field measurement technique has applications to a wide range of plasma topics.

Interactions:
University of Illinois, Electrical and Computer Engineering (M. Kushner)
Naval Research Laboratory, (M. Lampe, G. Joyce)
University of Iowa (J. Goree)
Technical University Eindhoven, Netherlands (G. Kroesen)
Baylor University (T. Hyde)
Wright Patterson Air Force Research Laboratory (B. Ganguly, A. Garscadden)

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Three invited talks. Physical Review Letter

Personnel Commitments for FY2002 to Nearest +/- 10%:
G. Hebner (50), M. Riley (50)
K. Greenberg, summer sabbatical (60), A. Boone, summer student (100)
M. Kushner, professor (10), V. Vihas, graduate student (100)

Authorized Budget (BA) for FY00, FY01, FY02:
FY00 BA $402 K **FY01 BA $378 K** **FY02 BA $370 K**

Laboratory Name: Sandia National Labs/NM
B&R Code: KC020105

FWP and possible subtask under FWP:
Energetic-Particle Synthesis and Science of Materials

FWP Number: SCW 1952

Program Scope:
Energetic-particles are used with other experimental tools and *ab-initio* theory to advance understanding of the atomic and nanostructural processes governing materials properties. This widely-ranging program continues to evolve and thereby address fundamental questions at the forefront of materials science. Currently, our experimental and theoretical studies are providing a unified mechanistic understanding of the important role of H in the newly emerging nitride semiconductors. Additionally, metals tailored at the nanoscale using energetic particles are allowing us to probe fundamental limits on strength and to extend mechanical-property scaling relationships into regimes of microstructural refinement not heretofore explored at a quantitative level. Previously in the program, important fundamental contributions were made in a number of areas including metal-gettering reactions in Si, hydrogen in metals, metastable icosahedral and amorphous phases, and implantation modification of materials.

Major Program Achievements (selected items over duration of support):
- In a series of theoretical and experimental papers dating from 1999, we have put forward a unified, fundamental understanding of the multifaceted behavior of H in GaN which, in a number of respects, goes beyond what has previously been achieved for any semiconductor.
- Through micromechanical testing of nanostructured alloys synthesized with energetic particles, we have demonstrated that Orowan scaling of strength in metals with precipitate dispersions can persist to particle sizes and separations approaching 1 nm, giving rise to strengths well above what has previously been achieved. Additionally, Hall-Petch scaling of strength in polycrystalline Ni has been shown to persist for grain sizes extending down to 10 nm, contrary to reports based on studies of less-ideal materials.
- In fundamental studies of metal gettering in Si which culminated in an invited review of the field in 2000, we identified new, exceptionally effective traps (cavities and B-Si precipitates) and developed an improved theoretical description of gettering behavior.
- Our extensive experimental and theoretical studies of H-defect and H-surface reactions, concluding with invited review articles in 1989 and 1992, provided a key scientific understanding the behavior of H in irradiated metals.

Program Impact:
- Our work on H in GaN illuminates the technologically critical issue of dopant activation in p-type material, to the degree the present BES program has spawned a new thrust within Sandia's solid-state lighting initiative to explore the implications for device processing.
- The understanding of grain-size and precipitation strengthening being developed here is important for micro-electromechanical systems, where limitations on the strength and hardness of metal components are constraining device design and performance.
- Even after a decade, the understanding of H-metal interactions developed in the present program continues to have impact on the handling of H-isotope recycling in fusion-reaction walls and in neutron-tube sources.

Interactions:
This program has included widely-ranging interactions with other laboratories [LANL, LBNL, ORNL, PNNL] and universities [UC-Berkeley, U. Wisc., U. Aarhus (Denmark), U. Canberra (Australia), U. Göttingen (Ger.)] as well as providing scientific insights benefiting Sandia missions (SS lighting, MEMS, fusion energy, neutron generators).

Recognitions, Honors and Awards (at least in part attributable to support under this program):
- Eighteen invited papers and presentations since 1995.
- The recent coupling and extension of this BES program to the solid-state lighting initiative was chosen as the (single) example of Sandia science to be presented at DOE's Sept. '02 LDRD review.

Personnel Commitments for FY02 to Nearest +/–10%:
S. M. Myers (coord.) 50%; D. M. Follstaedt 35%; S. J. Hearne 50%, J. A. Knapp 35%; C. H. Seager 20%; W. R. Wampler 25%; A. F. Wright 20%.

Authorized Budget (BA) for FY00, FY01, FY02:
FY00 BA $697 K **FY01 BA $637 K** **FY02 BA $631 K**

Laboratory Name: Sandia National Labs/NM
B&R Code: KC020105

FWP and possible subtask under FWP:
Advanced Growth Techniques and the Science of Epitaxy

FWP Number: SCW 1957

Program Scope: Development of advanced growth techniques and in situ diagnostics for the synthesis of improved thin film structures. The ability to measure the evolution of critical parameters such as surface morphology and film stress *as they develop* greatly expands our potential for understanding and controlling fundamental processes that determine nanoscale film structure and self-assembly.

Major Program Achievements (over duration of support):
Ion/surface interaction studies using multiple real-time diagnostics quantified surface defect production rates, surface defect transport and interactions, and kinetics of mesoscale pattern self-assembly.

Investigations of self-assembled heteroepitaxial semiconductor quantum dot using real-time stress sensing and light scattering showed how elastic repulsion determines evolution of dot arrays. Repulsion promotes spatial ordering, accelerates ripening kinetics, and enhances quantum dot phase transitions.

We made the first real-time measurements of stress evolution during III-nitride chemical vapor deposition, demonstrating the ability to measure, modify, and understand stress evolution of nitride heterostructures.

Comprehensive studies of stress generation during growth of polycrystalline and amorphous thin films resulted in a fundamental understanding of competing mechanisms that create stress during deposition, including a new model for growth flux-induced compressive stresses in polycrystals.

Program impact:
We have shown quantitatively how ion bombardment can tailor surface morphology and structure, providing a deterministic tool for film growth and surface science. Our comprehensive understanding of quantum dot self-assembly suggests strategies for controlling dot size and placement, relevant to nanoelectronics. Results of our III-nitride stress studies were utilized by device groups at Sandia to suppress fracture, enabling fabrication of one of the first UV vertical cavity surface emitting lasers. In polycrystalline films, our work demonstrates means by which deleterious stresses may be minimized. Finally, the stress sensor we developed for this project has been licensed for commercial production and is used in labs throughout Sandia and at more that two dozen institutions worldwide.

Interactions:
Brown University (Div. of Eng.); University of Virginia (Dept. of MSE); IBM Watson Research Center; MIT (DMSE); Arizona State University (Dept. of Physics and Astronomy); Harvard University (Div. of Appl. Science); University of Texas, El Paso (Dept. of Physics).

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
1994 award for Outstanding Sustained Research in Metallurgy and Ceramics.
Publications include: 1 Nature, 6 Physical Review Letters, 1 invited MRS Bulletin review, 2 book chapters.
More than 24 invited conference talks and 20 university colloquia since the inception of this project.

Personnel Commitments for FY2002 to Nearest +/- 10%:
Jerrold A. Floro, 80%; Steven Seel, 40%

Authorized Budget (BA) for FY00, FY01, FY02:
FY00 BA $308 K **FY01 BA $285 K** **FY02 BA $315 K**

Laboratory Name: Sandia National Labs
B&R Code: KC020202

FWP and possible subtask under FWP:
The Physics of Structured Semiconductors

FWP Number: SCW 1349

Program Scope Understand the physics of structured semiconductors from the quantum to the macroscopic level. The ultimate goal is to understand how structuring on the nanoscale produces new semiconductor-material properties: optical, electronic, transport and structural. When this is achieved, the community will be able to control the properties of individual electrons and photons to an unprecedented degree, at the level of the wavefunction. To this end, this program utilizes three approaches: 1. investigate fabricated quantum confined structures to probe the fundamental physics; 2. investigate self-assembled nanostructured semiconductors; and 3. investigate new semiconductor compounds, connecting electronic structure calculations to experimental measurements.

Major Program Achievements (over duration of support):
The fundamental understanding of tunneling between two-dimensional electron gas (2DEG) layers grown from compound semiconductor heterostructures was developed and then control over this physics was demonstrated in a double electron layer tunneling transistor (DELTT). Recently, we demonstrated high-mobility heterostructures produce new resistance oscillations. Grown from GaAs/AlGaAs heterostructures, a 2DEG had a low-temperature mobility in excess of 10^7 cm^2/Vs. This mobility indicates extraordinarily low disorder, which is required to probe the physics of electron interactions in low-dimensional nanoscale systems. Using these 2DEGs, a new class of Shubnikov-de Haas-like oscillations was discovered at low magnetic fields.

The parameter space that produces strong composition modulation in the growth of compound semiconductors was determined. An understanding of how the modulation structure depends on the stress state (tension versus compression) was then developed. For InAs/AlAs, a two-dimensional structure was formed; and by understanding how to selectively control which growth direction dominates, we were able to make InAs quantum wires and stacked quantum wires in order to assess the electronic structure arising from quantum confinement effects.

Sandia is one of the first groups to determine the effects on electronic band structure of defect in III-nitride semiconductors. Initial results were obtained using density functional theory (DFT) to understand dislocations in AlN. This work was extended to substitutional and interstitial impurities in GaN. Recent results gave atomic structures and formation energies of C in GaN as a function of growth stoichiometry and Fermi level. Discovery of a unique C-C complex has important implications which could limit the usefulness of carbon as a *p*-type dopant.

Program Impact:
Experiment and theory are combined to discover and understand some of the most exciting physics in compound semiconductor research today. This is achieved by understanding how to utilize nature to grow unique structures and then identify the physics of these structures. An example is the work of Simmons on the Double Electron Layer Tunneling Transistor (DELTT)

or the work of Wright on hydrogen in GaN. This impact continues with discovery of new resistance oscillations produced from quantum confinement in high-mobility heterostructures.

Interactions:
U. Florida, Karen Waldrip performed her thesis work on nitrides at Sandia.
NREL, studies in compositionally modulated structures (together with U. Houston and U. Michigan).
National High Magnetic Field Laboratory in Tallahassee, Florida and Princeton University.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Numerous invited talks at the American Physical Society Meeting and the Materials Research Society Meeting.
J. A. Simmons was made a fellow of the APS. Industry Week Technology of the Year award 1998 (DELTT).

Personnel Commitments for FY2002 to Nearest +/-10%:

M. P. Lilly 30%;	D. M. Follstaedt 30%	A. F. Wright 25%
J. L. Reno 25%	S. R. Lee 30%	D. D. Koleske 20%
J. A. Simmons 10%	E. D. Jones 10%	S. K. Lyo 10%

Authorized Budget (BA) for FY00, FY01, FY02:

FY00 BA $621 K	**FY01 BA $565 K**	**FY02 BA $520 K**

Laboratory Name: Sandia National Labs/NM
B&R Code: KC020202

FWP and possible subtask under FWP:
Atomistic Basis for Surface Nanostructure Formation

FWP Number: SCW 1951

Program Scope: Combine experimental measurements of the time-evolution of nanoscale surface features with detailed experimental and theoretical studies of how atoms and defects move and interact on surfaces to understand how atomic-scale kinetic processes control collective surface phenomena. By elucidating the new physics resulting from the interplay between the thermodynamic properties of surfaces and kinetic behavior of adsorbed atoms, we establish the scientific principles that govern the spontaneous formation and stability of nanostructures on surfaces.

Major Program Achievements (over duration of support):
1) New physical phenomena: Discovered important new mechanisms for processes on surfaces including Auger-induced electron and photon stimulated desorption, exchange-mediated surface diffusion, and vacancy-mediated surface diffusion. Acquired a physical understanding of a variety of surface phenomena including the relationship between the electronic structure and chemical activity of strained-metal overlayers, oxygen's surfactant effect on Pt(111) homoepitaxial growth, boron-induced stripe formation on Si(100), phase transitions on Si(111), and oxygen-induced etching of Si(100). Discovered and explained a remarkable self-assembly and pattern formation process for Pb atoms on Cu(111).
2) Quantitative determination of atomic processes on surfaces: Measured and calculated energy barriers for a variety of atoms, clusters, and defects diffusing on both metal and semiconductor surfaces. Showed how electric fields and impurity species can be used to manipulate atomic processes to tailor surface growth.
3) Technique development: Developed new experimental surface probes including pulsed-laser atom probe mass spectroscopy and atom-tracking scanning tunneling microscopy. Developed Density Functional Theory code for first-principles investigations of the energetics of atoms and defects on surfaces.

Program impact:
Research results have provided new insights on the microscopic origins surface chemical reactions, crystal and thin-film growth, surface phase transitions, and surface self-assembly. Experimental and theoretical probes have been adopted in other university and industrial research laboratories. Organized symposia and hosted conferences related to research. Research results have appeared in popular press (*Popular Science*, *Popular Mechanics*, *Science News*, *Wall Street Journal*, etc.)

Interactions:
University interactions include: University of Wisconsin at Madison, Rutgers University, University of Pittsburgh, Carnegie Mellon University, Penn State University, University of Twente, University of Texas at El Paso, New Mexico State University, University of New Mexico
Industry and government interactions include: Los Alamos National Laboratory, IBM Yorktown Heights, KFA-Julich.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Four BES/MS Awards; 1996 AVS Medard W. Welch Award (Feibelman); 1997 AVS Peter Mark Memorial Award (Swartzentruber); DOE Office of Energy Research's Young Scientist Award (Swartzentruber); 2001 Materials Research Society Prize (Bartelt), Fellows of the APS (Feibelman, Kellogg, Bartelt), Fellows of the AVS (Feibelman, Kellogg, Bartelt, Swartzentruber), numerous editorial boards, conference and symposium organizers, national and international scientific committee positions, and invited talks.

Personnel Commitments for FY2002 to Nearest +/- 10%:
G. Kellogg (50%), B. Swartzentruber (40%), P. Feibelman (30%).

Authorized Budget (BA) for FY00, FY01, FY02:

FY00 BA $485 K **FY01 BA $445 K** **FY02 BA $406 K**

Laboratory Name: Sandia National Labs/NM
B&R Code: KC020202

FWP and possible subtask under FWP:
Center for Integrated Nanotechnologies

FWP Number: SCW 3247

Program Scope:
The Center for Integrated Nanotechnologies (CINT), Project No. 02-SC-002-06, is a U.S. Department of Energy (DOE) line item project that is being carried out as a partnership between Sandia National Laboratories (SNL) and Los Alamos National Laboratory (LANL) to design and build a world-class user facility for research in nanoscale science. The project will construct a Core Facility in Albuquerque and a Gateway to Los Alamos Facility in Los Alamos. A Gateway to Sandia Facility will be developed using existing space and no new construction. The CINT Project will provide state-of-the art nanoscience experimental and theoretical tools and capabilities to be housed within the CINT Facilities.

Major Program Achievements (over duration of support):
The CINT Project was granted CD-1 authority in June, 2002. An architectural engineering firm has been contracted to for Title 1 design for the Core Facility. The contract was awarded on 8/8 and Title I work started on 8/18. Programming to verify the facility's space needs has been completed. Schematic design is underway. An Environmental Assessment is being prepared by a consultant under contract to NNSA/OKSO. Detailed schedule in place for Performance Specification development for joint Core/Gateway to Los Alamos EIR. Performance Specification development will began in November, 2002 with programming efforts supported by a Nanotechnology Laboratory consultant.

Program impact:
CINT's primary objective is to develop the scientific principles that govern the performance and integration of nanoscale materials, thereby building the foundations for future nanotechnologies. The distinguishing characteristic of the Center is its focus on exploring the path from scientific discovery to the integration of nanostructures into the micro and macro worlds. This path involves experimental and theoretical exploration of behavior, understanding new performance regimes and concepts, testing designs, and integrating nanoscale materials and structures. This Center will work closely with the other NSRCs to ensure that their discoveries are evaluated in the context of integrated functional systems. This approach offers a unique role for the DOE in support of the National Nanotechnology Initiative.

Interactions:
CINT has developed interactions with the other four DOE/NSRC as well as other nanocenters sponsored by the NSF and state and local initiatives.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
None

Personnel Commitments for FY2002 to nearest +/- 10%:
N/A

Authorized Budget (BA) for FY00, FY01, FY02:
FY00 BA $0 K **FY01 BA $225 K** **FY02 BA $550 K**

Laboratory Name: Sandia National Labs/NM
B&R Code: KC020202

FWP and possible subtask under FWP:
The Science of Electronic and Optical Interactions Between Coupled Nanostructures

FWP Number: SCW 40918

Program Scope:
This research project investigates the interactions between coupled nanoelectronic and nanophotonic structures. We are addressing the following general questions: What novel types of behavior—including collective behavior—ensue from different types of strong interactions—e.g. photon and electron tunneling, Coulomb, and exchange? How sensitive is the behavior to geometry, interaction strength, and temperature? How well can it be controlled and manipulated? What new methods of materials growth, patterning, and synthesis will enable creation of large, strongly interacting arrays of nanostructures? How can interfacing with the macro-world best be accomplished?
Four major thrusts are being investigated: (1) Interacting low-dimensional nanoelectronic structures; (2) Interacting nanophotonic structures; (3) Hybrid interactions between nanoelectronic and nanophotonic structures, in particular systems consisting of colloidal quantum dots embedded within photonic crystals; and (4) Interaction-driven self-assembly of nano-materials.

Major Program Achievements (over duration of support):
As part of our progress towards making an ultra-clean, strongly coupled electron-hole bilayer system, we have developed a technique for producing 2D layers in undoped quantum wells. These 2D hole and electron layers have record low densities and high mobilities.
Previous studies of 2D electrons have indicated that low density 2D systems might form a non-Fermi liquid state at low carrier density—i.e. a *metal-insulator transition* (MIT). Due to their cleanliness and record low density, in our layers we have shown that the apparent "transition" is instead due to conventional scattering mechanisms, and so can be understood within the framework of Fermi liquid physics. We obtain similar results on 2D hole systems in collaboration with Princeton.
We are investigating InAs quantum dot structures grown on *modulated templates*. The template is formed by self-assembled composition modulation of an InAs/AlAs superlattice on InP. In appropriate superlattices, two in-plane composition waves form and interfere to produce isolated InAs-rich columns. When InAs quantum-dot layers are deposited on the modulated template with a thin intervening barrier layer, AFM shows a nearly hexagonal pattern of dots on the surface that mimics the composition modulation pattern. The short modulation wavelength (~30 nm) thus induces an ordered, high-density ($1x10^{11}/cm^2$) array of quantum dots.

Program impact:
The development of ultra-high mobility and record low density 2D electron layers extends the range of physical regimes available to test fundamental condensed matter physics issues. For this reason, there is considerable interest in Sandia's AlGaAs/GaAs material, and we expect to be a major supplier for quantum transport efforts throughout the U.S. for many years to come.
Our results on the metal-insulator transition will have a major impact on this community, and on Fermi liquid and electron-electron interaction physics.
The ability to grow high density, ordered arrays of quantum dots may enable better quantum dot lasers, with lower current thresholds, higher efficiencies, higher powers, and wider spectral ranges.

Interactions:
Although this project is only about one year old, interactions already include Princeton, Caltech, Univ. of Utah, Arizona State, the National High Magnetic Field Lab, and the Univ. of Florida..

Recognitions, Honors and Awards (at least partly attributable to support under this FWP):
Numerous invited talks, including XXX (Mike, please fill in…)

Personnel Commitments for FY2002 to Nearest +/- 10%:

Mike Lilly, Mike Sinclair, Dave Follstaedt, Shawn Lin, LANL folks, UNM subcontract.

Authorized Budget (BA) for FY00, FY01, FY02:
FY00 BA $0 **FY01 BA $275 K** **FY02 BA $425 K**

Laboratory Name: Sandia National Labs/NM
B&R Code: KC020203

FWP and possible subtask under FWP:
Synthesis and Processing Center (CSP)

FWP Number: SCW 2939

Program Scope:
The DOE Center of Excellence for the Synthesis and Processing of Advanced Materials (CSP) is a distributed center for promoting coordinated, cooperative research partnerships related to the synthesis and processing of advanced materials. It was established by DOE's Division of Materials Sciences and Engineering, Office of Basic Energy Sciences and the DOE Laboratories in recognition of the enabling role of materials synthesis and processing to numerous fabrication- and manufacturing-intensive technologies. The participants include investigators from 12 DOE national laboratories, universities and the private sector. The Center has a technology perspective which is provided by a Technology Steering Group.

The current emphasis of the Center is on eight focused multilaboratory projects which draw on the complementary strengths of the member institutions in their ongoing research programs. These eight projects were selected on the basis of the following criteria: (1) scientific excellence, (2) clear relationship to energy technologies, (3) involvement of several laboratories, (4) existing or potential partnerships with DOE Technologies-funded programs, and (5) existing or potential "in-kind" partnerships with industry.

The member laboratories of the Center are: Ames Laboratory (Ames), Argonne National Laboratory (ANL), Brookhaven National Laboratory (BNL), Idaho National Engineering and Environmental Laboratory (INEEL), University of Illinois Frederick Seitz Materials Research Laboratory (UI/MRL), Lawrence Berkeley National Laboratory (LBNL), Lawrence Livermore National Laboratory (LLNL), Los Alamos National Laboratory (LANL), National Renewable Energy Laboratory (NREL), Oak Ridge National Laboratory (ORNL), Pacific Northwest National Laboratory (PNNL), and Sandia National Laboratories (SNL). The Center also includes appropriate university grant research and some industry participation.

The overall objective of the Center is,

"To enhance the science and engineering of materials synthesis and processing in order to meet the programmatic needs of the Department of Energy and to facilitate the technological exploitation of materials".

Funds in this program support administrative costs, publications costs, expenses of the Center's Technology Steering Group and meeting costs.

Authorized Budget (BA) for FY00, FY01, FY02:
FY00 BA $103 K **FY01 BA $86 K** **FY02 BA $80 K**

Laboratory Name: Sandia National Labs/NM
B&R Code: KC020301

FWP and possible subtask under FWP:
Cooperative Phenomenon in Molecular Nanocomposites

FWP Number: SCW 11975

Program Scope: We seek to establish key scientific principles needed to design and fabricate three- dimensional nanocomposite architectures that combine the unique functions and capabilities of organic molecular assemblies with robust, stable inorganic scaffolds. Our research is focused on the interplay between architectures of multiple, hierarchical length scales, cooperative molecular responses, and the resultant overall properties of this new class of organic-inorganic composites. We approach this objective by synthesizing model molecular composites via self-assembly techniques, and by applying unique diagnostic and modeling tools to monitor structure and response directly.

Major Program Achievements (over duration of support):
Self-assembly of conjugated polymer/silica nanocomposite films with hexagonal, cubic, or lamellar mesoscopic order was achieved using polymerizable structure-directing agents. The nanostructured inorganic host alters the diacetylene polymerization behavior, and the resulting nanocomposite exhibits unique optical properties in response to thermal, chemical, and mechanical stimuli.
We have devised a general, solution-based approach to building large self-assembled silica-based structures with control of crystal size, orientation, and morphology over many length scales. Such self-assembled hierarchical ordering is found in composite biomaterials but is mostly absent in synthetic materials.
Nanocomposite architectures of light-harvesting molecules have been demonstrated. Silica scaffolds were used to spatially organize porphyrin molecules that photo-catalyzed the growth of metallic particles and nanowires within the mesoporous silica structures.
Unique molecular functionality has been demonstrated self-assembled films. One case is poly-n-isopropylacrylamide films that thermally switch between hydrophilic and hydrophobic states, thus allowing reversible protein adsorption. Another case is receptor-functionalized lipid membranes that have been observed at the nanoscale to reorganize as a response to chemical recognition events at the membrane surface.

Program impact:
This program has stimulated progress in the understanding of the formation and function of biological-inspired composite materials and the dynamic behavior of molecular assemblies in silica structures.

Interactions:
Chemical Engineering, University of California, Davis
Chemical and Materials Engineering, Arizona State University
Chemical Engineering, Tulane University
Chemistry, University of California, Los Angeles

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
DOE E. O. Lawrence Award in Material Science to C. Jeffrey Brinker (2002)
Lecture at International Vacuum Congress/American Vacuum Society Symposium (2001) by D. Y. Sasaki.
Cover article for *Langmuir* April 4, 2002 issue, by D. Y. Sasaki

Personnel Commitments for FY2002 to Nearest +/- 10%:
A. Burns (project manager 40%), B. Bunker (30%), D. Sasaki (30%), J. Brinker (20%), J. Liu (20%)

Authorized Budget (BA) for FY00, FY01, FY02:
FY00 BA $0 **FY01 BA $533 K** **FY02 BA $504 K**

Laboratory Name: Sandia National Labs/NM
B&R Code: KC020301

FWP and possible subtask under FWP:
The Science of Heteroepitaxial Structural Evolution (formerly CVD Sciences)

FWP Number: SCW 1954

Program Scope:
The scope of the program has recently changed to emphasize understanding of the following scientific challenges in heteroepitaxy: Surfactant effects on nanostructure nucleation and evolution; Kinetics of crystal facet evolution; and Stress relaxation mechanisms. This work will combine state-of-the-art experimental tools with theory and modeling. The latter includes first principles theory, theory of chemically reacting flows, and modeling of the energetics and kinetics of facet-dependent crystal growth. We will extensively use techniques such as MOSS (Multibeam Optical Stress Sensor), AFM, STM, SEM, TEM, and x-ray diffraction to study the evolution of surfaces and relaxation mechanisms.

Major Program Achievements (over duration of support):
Unprecedented understanding of CVD reaction mechanisms through a combination of modeling and in situ diagnostics of the coupled fluid-flow, gas-phase and surface chemistry. CVD chemistry systems that have been investigated include: Si, SiO_2, GaAs, GaN, diamond, and W.

We developed a broad suite modeling techniques and software (Chemkin) to conduct our basic research into CVD reaction mechanisms and kinetics. This reactor modeling software is now a commercial product of Reaction Design, Inc. (San Diego, CA), with over 250 license holders.

Rotating-disk reactor was developed as an ideal test-bed for studying CVD chemistry. An outgrowth of this fundamental research was a partnership with Emcore Corp. to design their flagship Enterprise-400 reactor.

Filmetrics, Oriel, and Emcore Corporations have commercialized in situ growth monitoring probes that were developed under this program. The growth rate monitor was a winner of a R&D 100 Award.

Program impact:
We have developed experimental tools and theoretical techniques that led to the first detailed understanding of the fundamental mechanisms of CVD. This research has had a clear impact on CVD Science. Our initial journal article on CVD modeling was listed as one of the 20 most-cited papers in the field of Materials Science within the previous 20 years (from the Institute for Scientific Information). We have also made a significant contribution to the U.S. technology base through commercialization of many of the research tools developed in the program (listed above), and through research partnerships with industry (Hewlett-Packard, Motorola, Emcore, GE, SEMATECH, Texas Instruments, Norton, United Technologies).

Interactions:
Numerous interactions with U.S. industry, listed above. Collaborations with universities include: Caltech, Colorado State University, Colorado School of Mines, SUNY Buffalo, and University of Florida.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Five BES awards for Outstanding Scientific Accomplishment (1984), Sustained Outstanding Research (1992), and Significant Impact for DOE Related Technology (1986, 1987, 1994). R&D 100 Award (1997).

Personnel Commitments for FY2002 to Nearest +/- 10%:
Michael E. Coltrin (project leader) 50%; J. Randall Creighton, 50%; George Wang, 50%; Daniel D. Koleske, 20%; Jeffrey Cederber, 20%, Stephen R. Lee, 10%.

Authorized Budget (BA) for FY00, FY01, FY02:
FY00 BA $597 K **FY01 BA $550 K** **FY02 BA $507 K**

Laboratory Name: Sandia National Labs/NM
B&R Code: KC020301

FWP and possible subtask under FWP:
Dipolar Nanocomposites

FWP Number: SCW 2254

Program Scope: The goal of this program is to develop and investigate a class of complex materials we call dipolar nanocomposites, that consist of superparamagnetic (or dielectric) nanoclusters organized into structures of variable dimensionality in a solid matrix, using both directed and self-assembly techniques. In these materials, the formation of structure and/or the physical behavior is dominated by collective classical interactions. In essence, each superparamagnetic particle can be viewed as a giant atom, with a giant spin. However, these giant spins interact with each other solely through classical dipolar interactions, whereas real magnetic atoms have quantized magnetic spins that interact via quantum mechanical exchange coupling *and* by dipolar interactions. Exchange coupling causes spin alignment and ferromagnetism, and the relatively weak dipolar interactions lead to domain formation. Dipolar nanocomposites of superparamagnetic clusters should have many of the features of ferromagnetic materials, despite the lack of exchange coupling, and should exhibit "superferromagnetism" as these domains grow and rotate. Because of the low energy scale of the dipolar coupling, large susceptibilities can be expected. Our approach is to understand the physical properties of isolated nanoclusters, how single nanocluster properties change in complex particle assemblies, and how these nanoclusters interact to produce the collective properties observed in nanocomposites.

Major Program Achievements (over duration of support):

- Development of heterodyne triaxial field magnetic mixing techniques that enable an agglomerated suspension of superparamagnetic particles to be resuspended, then structured into a high susceptibility state by turning off selected field components. For strongly interacting nanoparticles magnetic agglomeration is inevitable.
- Demonstrated that it is possible to structure a suspension of superparmagnetic particles into sheet-like structures that have a giant susceptibility anisotropy.
- Demonstrated that the susceptbility anisotropy can be 10:1 for superparamagnetic particle structures, far larger than can be obtained from multidomain particles.
- Developed a self-consistent Brownian Dipole Dynamics code to simulate the magnetism of superparamagnetic particle agglomerates. This parameter-free code predicts many things that are found in experiments of structured DPNs, such as the anisotropy in the spin blocking temperature, extremely large susceptibility anisotropies, and the reduction of the susceptibility below the blocking temperature.
- Developed a noise-free method of simulating the equilibrium magnetism of DPNs we call Langevin Dipole Dynamics. This code is also several orders of magnitude faster than the Brownian Dynamics code.
- Demonstrated a novel, deterministic method of finding the magnetic ground states of superparamagnetic particle arrays and agglomerates, using a controlled polarization catastrophy. Due to the extremely high density of states, this is an extremely difficult problem that normally requires techniques such as simulated annealing.
- Synthesis of high saturation magnetism Fe nanoparticles.

Program Impact: We have shown through simulation and experiment that it is possible to greatly enhance the magnetic properties of superparamagnetic particle assemblies through the control of suspension structure with triaxial magnetic fields. These enhancements are far in excess of those that can be achieved with multidomain particles.

Interactions: DOE Center for Synthesis and Processing project on, Nanomagnets; Carnegie Mallon Univ. (S. Majetich)

Recognitions, Honors and Awards: Editorial Board of the Journal of Chemical Physics. DOE "Chunky Bullet" award; numerous invited papers.

Personal Commitments for FY 2002: J. E. Martin (20%), E. Venturini (20%), D. Huber (20%)

Authorized Budget (BA) for FY00, FY01, FY02:

FY00 BA $239 K **FY01 BA $210 K** **FY02 BA $200 K**

Laboratory Name: Sandia National Labs/NM
B&R Code: KC020301

FWP and possible subtask under FWP:
Synthesis and Processing of Nanoclusters for Energy Applications

FWP Number:SCW 5828

Program Scope: Development and application of advanced synthesis and processing methods for producing metal and semiconductor nanoparticles of interest to DOE energy technologies. Our program pioneers the use of advanced analytical characterization tools such as liquid chromatrography to provide feedback for new nanocrystal synthetic protocols and studies the optical, catalytic, magnetic, and electronic properties of these materials. Examples of new technologies enabled by our work include nanophosphors for solid state lighting, nanosize photocatalyts for oxidation of toxic chemicals in water, and magnetic materials for inductors, and information storage.

Major Program Achievements (over duration of support):
The first demonstration of size-dependent, highly efficient, visible light driven photooxidation of chlorinated aromatic chemical using nanosize MoS2 semiconductors.
The first room T synthesis of nanocrystalline Si and Ge in high yield with size tunable visible luminesence.
The first demonstration of visble light emission from ultrasmall metals such as Au and Ag with visible plasmons.
The development and application of high resolution size-exclusion liquid chromatography (HRSEC) to establish critical, magic size, cluster abundances in systems of Au, Ag, Pt, Pd, and Rh, and the demonstration of unique molecule-like optical features unique to such ultrasmall,1-3 nm clusters.
The first development of new NIR emitting materials such as PbS, PbSe, HgS and HgSe which have intense invisible emission vastly exceeding any conventional material.
The demonstration of the importance of surface restructuring in nanosize Co, Ni, and Fe and the achievement of greater than bulk magnetic saturation in nanosize Co by suitable surface passivation and aging.

Program impact:
New types of nanomaterials such as MoS2, Si, CdS, CdSe and Co will enable the development of new technologies, and rapid characterization tools such as HRSEC for quality control, and rapid synthetic feedback. Recent examples include the ability to tune emission PL throughout the visible in CdS by variation of only the interface chemistry, intense NIR emission from PbS and PbSe, and new nanocatalysts for fuel production, FeS2, and environmental remediation, MoS2.
Interactions:
U. of Birmingham (Dr. Richard Palmer)-Nanopatterning of clusters for electronic applications
Sandia National Lighting Initiative-Development and characterization of new nanocluster-based phosphors.
Lawrence Livermore National Labs (Dr. Tony van Buuren)-Bandgaps of nanosize Si and MoS2 studied using synchrotron based spectroscopies.
Lawrence Livermore National Labs (Dr. Arthur Dennison)-Positron emission spectroscopy of nanosize Au, Ag and Au/Ag clusters.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
BES award for significant implications for DOE technologies, (1996).
Appointment as honory full professor, Dept. of Physics, U. of Birmingham, U.K. (1998)
Numerous international invited talks and papers in nanoscience.

Personnel Commitments for FY2002 to Nearest +/- 10%:
Jess Wilcoxon (65%), Eugene Venturini (15%), Paula Provencio (10%).

Authorized Budget (BA) for FY00, FY01, FY02:
FY00 BA $300 K **FY01 BA $275 K** **FY02 BA $270 K**