

FWP Title: Defects and Defect Processes in Ceramics
FWP Number: 18048

Pacific Northwest National Laboratory
B&R Code: KC020102

Program Abstract:

This multidisciplinary research effort investigates equilibrium and non-equilibrium atomic-level defects and defect processes in ceramics. Experimental and computational methods are synergistically integrated to study defects, including point defects, dopants, and gas atoms, and the dynamic processes associated with defect formation and migration, defect-defect interactions, and the evolution of nanostructures and phase transformations under different environmental conditions. A variety of processing, ion-implantation, and irradiation techniques are utilized to introduce atomic-level defects in ceramic oxides, carbides and nitrides. Defect configurations, properties, interactions, and kinetics of defect processes are experimentally investigated as functions of temperature, time and environmental conditions using ion channeling, electron microscopy, optical and X-ray spectroscopies, nuclear magnetic resonance, and electrical property measurements. Density functional theory, *ab initio* molecular dynamics, classical molecular dynamics, and kinetic Monte Carlo techniques are used to study the formation and migration of defects and the dynamics of defect interactions, nanostructure evolution, and phase transformations. The objective is to develop fundamental understanding and models of atomic-level defects, defect/property relationships, and dynamics of defect processes in ceramic structures that support the development of predictive models of materials behavior over multiple length and time scales under extreme conditions.

Program Impact:

Highly integrated, multidisciplinary experimental and computational effort has provided globally-adopted scientific understanding, models, defect energetics, and interaction potentials for defects and irradiation effects in ceramics. The co-siting of a major experimental capability (ion accelerator), computational resources and expertise has led to this project becoming an international research leader and partner that provides collaborative ion-beam irradiation opportunities, validates simulation models, provides computational models to support experimental interpretations, is a sought after collaborator by both experimental and computational single investigators and research teams, both nationally and internationally, and provides training to both experimental and computational students. This project has provided or demonstrated new experimental capabilities, such as for studying single ion events and in situ optical characterization, new characterization approaches, and new computational methods, such as for studying charge transfer and redistribution during ion solid interactions and high-pressure phase transformations. This project has provided predictive models applicable to ion-irradiation effects, development of radiation tolerant materials, long-term storage of actinide waste forms, and performance of nuclear materials. In FY09, this project published 28 peer-reviewed journal articles, provided 19 invited presentations at scientific conferences, workshops, universities, and institutions; and hosted a visiting scientist and several graduate and undergraduate students.

FY 2009 Authorized Budget: \$1,009k

Program Personnel Supported in FY2009 to Nearest +/- 10% FTE:

W.J. Weber, PI (60%); R. Devanathan, PI (50%); Y. Zhang, PI (20%); F. Gao, PI (30%); W. Jiang, PI (60%); P. Edmondson, PD (20%); H. Xiao, PD (30%); J. Yu, PD (50%); D. Chen, Student (25%)

Interactions: (limit to current interactions and collaborations)

Experimental Studies – R.C. Ewing, M. Lang (Univ. Mich.); J. Lian (RPI); F. Namavar (Univ. Nebraska Medical Center); L.A. Boatner (ORNL); I.-T. Bae (SUNY Binghamton); H. Wang (Texas A&M Univ.); M. Toulemonde (GANIL, France); T. Wiss (ITU, Germany); G. Baldinazzi, D. Simone (CEA-Saclay, France); L. Thome (Univ. Orsay, France); M. Ishimaru (Osaka Univ., Japan); J. Jagielski (Inst. Elect. Mater. Tech., Poland)

Computational Studies – L.R. Corrales (Univ. Arizona); A. Chartier, J.-P. Crocombette, L. Van Brutzel (CEA-Saclay, France); M. Posselt (Res. Ctr. Dresden, Germany); J. Du (Univ. N. Texas); J.D. Gale (Curtin Univ., Australia); Z. Wang, X. T. Zu (Univ. Elect. Sci. & Tech. of China); D. Duffy (Univ. Coll. London)

Related Project URL: (none)

FWP Title: Exploring Radiation Damage Resistance of Nanoscale Interfaces Pacific Northwest National Lab
FWP Number: 53154 **B&R Code: KC020102**

Program Abstract:

The objective of this research is to rigorously test the hypothesis that internal interfaces can be manipulated at the nanoscale to enhance recombination of radiation-produced defects to dramatically reduce radiation damage without compromising other physical and mechanical properties. This hypothesis has never been rigorously tested and there has never been a fundamental study of radiation damage at interfaces that encompasses the wide range of interface types and structures proposed here. In this project we seek to 1) understand defect absorption at interfaces as a function of interface character and properties, 2) determine interface ability to adsorb and delocalize defects to promote recombination, and 3) determine interface stability and evolution under irradiation, including the saturation limit for defect absorption. The work consists of integrated experiments and modeling of a range of interfaces to determine how variation in interface properties can affect defect absorption and recombination.

Program Impact:

Proposed fundamental research is aligned with two of the principal focus team research areas within the Materials Sciences and Engineering Division of BES; these areas encompass new approaches to improve materials performance through innovative interfacial design and modification, and mechanical behavior of materials and radiation effects. The project also is aligned with resident research activities at PNNL including PNNL's laboratory-level research project, the Transformational Materials Sciences Initiative, which supports mission-oriented laboratory research and strategies pursuant to energy and environmental scientific grand challenges. Synergies with existing BES projects at the laboratory also have been identified. These include WJ Weber's project on ion irradiation effects in materials and SA Chambers project on interfacial design and modification in oxide films. Productive scientific interactions across project boundaries are routinely registered at this laboratory and illustrate one of the strengths for supporting fundamental materials science research activities here. Proposed research is anticipated to provide new information on the role of tailored microstructures on radiation damage resistance.

FY 2009 Authorized Budget:

\$600k (new start in September 2009).

Program Personnel Supported in FY2009 to Nearest +/- 10% FTE:

Only minor staff support in FY2009 due to September start date. Projected personnel supported in FY2010 include R.J. Kurtz (30%), H.L. Heinisch (25%), S.A. Chambers (5%), T. Kaspar (30%), A.G. Joly (30%), R.M. Van Ginhoven (35%), V. Shutthanandan (20%), and C. Wang (20%).

Interactions: Joint research interactions were initiated with the University of California Berkeley on positron annihilation studies of ion-induced radiation damage at tailored interfaces (Prof. Brian D. Wirth plus a part-time ost doctoral researcher). Long-standing contacts within the fusion materials research community such as Prof. G. Robert Odette at University of California Santa Barbara, Prof. Nasr M. Ghoniem at University of California Los Angeles, and Dr. Roger Stoller at Oak Ridge National Laboratory will also be consulted during the course of this program.

Related Project URL: (none)

FWP Title: Crack-Tip Mechanisms Driving Environmental Degradation
FWP Number: 56909

Pacific Northwest National Lab
B&R Code: KC020102

Program Abstract:

First-of-a-kind, discovery-based research is being conducted to explain environmental degradation mechanisms through atomistic measurement and modeling of interfacial reactions occurring at buried crack tips. Oxidation at liquid-solid, gas-solid and solid-solid interfaces will be evaluated to establish basic processes leading to grain boundary degradation. Our proposed research builds on recent analytical transmission electron microscopy (ATEM) measurements revealing unexpected nanometer-scale crack opening and oxidation reactions driving intergranular (IG) cracking of LWR structural alloys in service. ATEM measurements have also shown dramatic compositional changes and eventual nanoporosity at the metal grain boundary leading the crack tip. Kinetic development of such features can only be explained by oxidation-induced vacancy injection. Collective evidence and analyses have suggested that IG penetrative degradation can advance in many corrosion-resistant alloys by selective grain-boundary oxidation even at low temperatures. Direct mechanistic links have been made among degradation of corrosion-resistant structural alloys in water, supercritical-water and high-temperature gaseous environments spanning a temperature range from 300 to 1000°C. These measurements and observations are generally inconsistent with continuum mechanics and electrochemical models of environmental degradation and point toward the need for atomic and molecular level understanding of the processes.

Program Impact:

Project funding and research activities were initiated in September 2009. The proposed research will produce revolutionary advances in our understanding of interfacial oxidation and material degradation processes for current and advanced nuclear reactor systems. It deals with two of the four major topics identified in the recent BES workshop on *Basic Research Needs for Advanced Nuclear Energy Systems*: interfacial behavior under extreme environmental conditions and understanding nanoscale interactions under extreme conditions. The buried crack tip creates a unique situation with extreme environmental and material conditions of temperature, chemistry, radiation, stress and strain. As a result, this research also deals with many issues identified in the BES Workshop on *Basic Research Needs for Materials under Extreme Environments* requiring new understanding regarding the most fundamental atomic and molecular origins of materials failure. Basic oxidation and degradation processes have far-reaching applications in a wide range of advanced energy applications where corrosion-resistant structural alloys are required for reliable performance.

FY 2009 Authorized Budget:

\$655k (new start in September 2009).

Program Personnel Supported in FY2009 to Nearest +/- 10% FTE:

Only minor staff support in FY2009 due to September start date. Projected personnel supported in FY2010 include S.M. Bruemmer (25%); K.M. Rosso (25%); K.F. Ferris (15%); C. Wang (25%); D.R. Baer (15%); L.E. Thomas (15%); M. Olszta (35%); and C.F. Windisch, Jr. (15%).

Interactions:

Joint research interactions were initiated with the University of Michigan (Prof. Gary Was) on grain boundary oxidation and Northwestern University (Prof. David Seidman) for atom-probe tomography experimentation. Contacts have also been established with the University of Idaho (Prof. You Qiang) and General Electric Global Research (Dr. Peter Andresen) for nanoparticle synthesis and high-purity alloy processing, respectively.

Related Project URL: (none)

FWP Title: Electronic & Magnetic Properties of Doped Oxide Films Pacific Northwest National Laboratory
FWP Number: 10122 B&R Code: KC020105

Program Abstract:

The broad range of electronic and magnetic properties exhibited by metal oxides can be extended through selective doping. Epitaxial film growth allows an unprecedented level of control over the doping process, particularly when layered structures are sought. Our aim is to utilize oxygen plasma assisted molecular beam epitaxy (OPAMBE) and off-axis pulsed laser deposition (OAPLD) to synthesize near-perfect epitaxial films and layered structures with uniform and spatially confined dopant distributions. The overarching goal is to create and investigate well-defined and well-characterized oxide structures in order to elucidate the effect of different doping schemes on magnetic, electronic, optical and multiferroic properties. In addition to a multi-faceted experimental approach, we employ state-of-the-art electronic structure calculations to predict structures and energies in select systems, as well as to assist in interpreting experimental results. This research significantly deepens our fundamental understanding of doped oxides, as well as shedding light on the feasibility of using doped oxides to advance the fields of oxide electronics and spintronics.

Program Impact:

The strength of this program is in its multi-disciplinary approach that is enabled by the extraordinary laboratory infrastructure afforded by being located in the Environmental Molecular Sciences laboratory (EMSL) at PNNL. The PNNL team consists of experts in epitaxial growth, x-ray photoelectron spectroscopy (XPS), x-ray absorption spectroscopy (XAS), optical spectroscopy, x-ray diffraction (XRD), Rutherford backscattering spectrometry (RBS), transmission electron microscopy (TEM), scanning probe microscopy (SPM), electronic transport, magnetometry, and solid-state theory. Within the EMSL, we have access to all the experimental capabilities needed to carry out this research except for synchrotron radiation x-ray absorption, which is done in collaboration with Steve Heald at the Advanced Photon Source. This work is significant to DOE concerns in that it focuses on advanced materials that may be useful for applications including the development of more energy and time efficient digital circuitry (including the possibility of semiconductor spintronics and quantum computing), the use of oxides as semiconductors for more energy-efficient analog electronics, and coupling solar energy to thermodynamically unfavorable processes such as water splitting to make hydrogen (via synergistic overlap with a program funded by BES Chemical Sciences for which Chambers is co PI).

FY 2009 Authorized Budget (New BA): \$ 750k

Program Personnel Supported in FY2009 to Nearest +/- 10% FTE

Scott Chambers – PI (film growth, XPS, program oversight) 55%; Timothy Droubay – co PI (film growth, XPS, magnetometry, equipment maintenance) 40%; Tiffany Kaspar – co PI (film growth, SPM), 45%; Joe Ryan and John McCloy – PNNL scientists (transport) 35%; Greg Exarhos – PNNL scientist (optical spectroscopy), 10%; V. Shutthanandan – PNNL scientist (RBS), 10%; Weilin Jiang – PNNL scientist (XRD), 10%; Chongmin Wang - PNNL scientist (TEM), 10%; Peter Sushko - PNNL scientist (solid-state theory); 10%; Liang Qiao – PNNL postdoc who started midyear (film growth), 55%. Lisa J. Wang (SULI undergraduate student, ZnO film modification), 10%.

Interactions: (limit to current interactions and collaborations)

Daniel Gamelin - University of Washington
Steve Heald - Argonne National Laboratory
Andreas Ney - University of Essen-Duisburg-Essen
Jim Zuo - University of Illinois at Urbana-Champaign
Torgny Gustafsson and Eric Garfunkel - Rutgers University
Harold Hwang - University of Tokyo
Jochen Mannhart - University of Augsburg
Ivan Petrov – University of Illinois at Urbana-Champaign

Related Project URL: (none)

FWP Title: Molecularly Organized Nanostructural Materials
FWP Number: 12152

Pacific Northwest National Laboratory
B&R Code: KC020105

Program Abstract:

The overall goal of this project is to investigate self-assembly and controlled nucleation and growth for synthesizing nanostructured materials with controlled three-dimensional architectures and desired crystalline phases and pore structures. New multiphase self-assembly approaches have been developed to prepare a new class of multifunctional, multicomponent materials with well-controlled architectures on the nano- and microscales using both molecular scale building blocks such as block copolymers and metal oxide precursors and nanoscale building blocks such as graphene sheets. These materials exhibit exceptional capacity and stability for energy storage applications. Computational tools and state-of-the-art NMR techniques are being developed to understand the self-assembly processes and the structures of the materials.

Program Impact: Biological systems abound with nanocomposites with well-controlled architectures based on multiscale and multifunctional building blocks. In contrast, traditional approaches for making such materials mostly rely on mechanical or chemical mixing which usually produces a random distribution of the constitutive phases. This project explores a new strategy to integrate controlled nucleation and growth and three-dimensional self-assembly processes to achieve precise structural control in complex multicomponent materials. This approach points to a new direction for self-assembly using multiple phases and multilength building blocks. To illustrate this approach, highly conductive graphene sheets, which provide the conductive path and mechanical stability to the overall structure, and polymers and ceramic precursors, are used as the starting materials. The graphene sheets are dispersed in the hydrophobic domains of surfactant molecules or polymers. The polymer, graphene sheets and metal oxide precursors self-assemble into ordered three-dimensional composites structures. The metal oxides are then crystallized between the graphene sheets as controlled by the functional head groups of the surfactants, forming a well-dispersed metal oxide and graphene nanocomposite that shows significantly better conductivity and stability than conventional nanocomposites and carbon composite materials for energy storage applications.

The development of well-controlled nanocomposite materials has important implications for next generation, multifunctional energy storage and conversion technologies in which DOE is interested. A wide range of molecular precursors for polymer and ceramic materials, and a range of nanoscale materials including nanoparticles, nanorods (nanotubes) and nanosheets, can be used for similar self-assembly processes. These materials also provide an ideal platform to study the fundamental molecular reactions that drive molecular templating, interface controlled nucleation and growth, and 3D self-assembly. The research involves a multi-disciplinary team of molecular chemists (Thallapally), materials scientists (Liu, Lee), computer scientists (Sushko) and spectroscopy experts (Exarhos, Wang). The expertise of device fabrication and testing facilities established through DOE's applied programs at PNNL also played a critical role in helping the BES project identify the target materials structures and properties, and in validating the results and the approaches.

FY 2009 Authorized Budget (New BA): \$ 650k

Program Personnel Supported in FY2009 to Nearest +/- 10% FTE

J. Liu, PI (new) 10%; G.J. Exarhos, co-PI 40%; L-Q Wang, co-PI, 50%; Y. Shin, co-PI, 40%; M. Sushko, co-PI (new) 25%; P. Thallapally, co-PI (new) 10%; Y.J. Lee, postdoc (new) 5%.

Interactions: (limit to current interactions and collaborations)

Igor L. Moudrakovski, Steacie Institute For Molecular Sciences, NRC-Canada (HP ^{129}Xe NMR porosity studies); Brian Saam, Physics Dept., Univ. of Utah (^{129}Xe NMR polarizer development); Ilhan Aksee, (Princeton University (synthesis of graphene-based materials).

Related Project URL: (none)