Laboratory Name: National Renewable Energy Lab
B&R Code: KC02.0103

FWP and possible subtask under FWP:
Overcoming the doping bottlenecks in semiconductors

FWP Number:
ERWER0K

Program Scope:
The objective of the project is to understand doping limits in various semiconductors and to propose ways to overcome these limits, which is essential to the design of a wide range of new semiconductor devices such as high-efficiency solar cells, blue and UV LEDs, lasers and detectors, next-generation integrated circuits, spintronics, and technology employing nanomaterials.

Major Program Achievements (over duration of support):
Developed a theory for equilibrium doping from which one can predict the doping properties of a wide range of semiconductors and insulators. Provided systematic approaches to overcome doping difficulty in semiconductors. A number of recent important experimental observations are explained, which include (i) ultrahigh doping of silicon, (ii) p-type conductivity of zinc oxide, (iii) high nitrogen solubility and clustering in gallium arsenide, (iv) p-type and bipolarly dopable transparent conducting oxides, (v) n-type diamond, and (vi) defects and doping of quantum dots. Band structure engineering by defect control represents another important achievement. The studies of oxygen induced direct-gap, visible light-emitting silicon, band gap tuning by hydrogen and Si in gallium arsenide nitride, and icosahedral symmetry through twinning in silicon nanostructures have added new dimensions to the project.

Program impact:
Overall, our studies provide insights on the microscopic origin of the doping limits in semiconductors, extend the physics of semiconductor point defects into the non-equilibrium growth regime, provide new approaches to overcome the doping limits, and suggest new ways to modify the properties of the host materials. We are recognized as a leader in the theoretical study of defects in semiconductors, as evidenced by more than 10 invited talks given in international conferences and schools in FY2007 and selection as session and conference chairs in international conferences. Published more than 70 papers, including 20 Physical Review Letters since FY00. Nature's "Materials Update" had a feature article on Aug. 8, 2002 about our proposal of direct-gap, light-emitting silicon.

Interactions:
Internal - Materials and Computational Sciences Center; National Center for Photovoltaics.
External - University of California, Santa Barbra, Lawrence Berkeley National Laboratory; Wright State University, Institute of Semiconductor Physics (CAS), Suranaree University of Technology.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Given over 40 invited talks in international conferences; Published 5 Review Articles since 2000.
DOE/BES Chunky Bullet Award, 2002
Fellows of American Physical Society, Su-Huai Wei, Shengbai Zhang

Personnel Commitments for FY2007 to Nearest +/- 10%:
Su-Huai Wei (Principal Investigator) 8% ; Shengbai Zhang 2%
Hong-Jun Xiang (post-doc) 100%
Lixin Zhang (post-doc) 100%
Juarez L. F. Da Silva (post-doc) 100%
Demien West (post-doc) 50%

Authorized Budget (BA) for FY05, FY06, FY07:
FY05 BA $390,000 **FY06 BA $374,000** **FY07 BA $382,000**

Laboratory Name: National Renewable Energy Lab
B&R Code: KC020103

FWP and possible subtask under FWP:
Novel Ordered Semiconductor Alloys

FWP Number:
ERWER20

Program Scope:
The research on this project involving ordered semiconductor alloys combines experimental and theoretical efforts aimed at understanding long-range order in isovalent semiconductor alloys. The project includes: (i) MOCVD growth of III-V alloys such as GaP/InP, growth of hybrid organic-inorganic superlattices (ii) Raman, modulation reflectance, photoluminescence, NSOM, Magneto-PL and reflectance-difference spectroscopy studies of ordering in the above systems, and (iii) first-principles theoretical studies of surface-induced, epitaxially-induced and bulk ordering in various alloys as well as on the electronic bandstructure changes and lattice dynamics changes induced by ordering. The project includes structural studies based on transmission electron diffraction and X-ray scattering for determining the order parameter, thermal expansion coefficient, and involves use of DOE synchrotron facilities.

Major Program Achievements (over duration of support):
Developed the concept of partial ordering, statistical distribution function and order parameter, orientational superlattices, effective mass anisotropy, pyroelectric behavior and spontaneous electric fields. Developed theoretical models for surface induced ordering. First structural and electronic measurements of order parameter. Developed ability to tailor order parameter and consequent electronic properties. Developed the understanding of the lattice dynamics and phonon spectrum of ternary alloy GaInP through control of order parameter. Developed the understanding of the influence of microstructure on the optoelectronic properties of the spontaneously ordered alloy. This work led to the first experimental demonstration of amphoteric (negative and positive) refraction at an orientational domain boundary, the first demonstration of giant tuning of bandgaps and zero thermal expansion in hybrid semiconductors.

Program impact:
Almost all the present understanding of the electronic properties of spontaneously ordered semiconductor alloys has been pioneered by this program. This understanding is now being exploited for engineering advanced solar cells, HBT transistors for cellular communications, and for novel polarization sensitive optical devices, as well as for providing insights into the exciting phenomenon of negative refraction

Interactions:
University of Houston (S.C. Moss), X-ray and synchrotron studies of order parameter.
Rutgers University (J. Li), Novel Hybrid organic-inorganic superlattices
NHFML-Florida State University, High Field Magneto-PL Studies of Ordered Alloys
Univ. of Erlangen (G. Doehler), Polarization sensitive devices based on ordered alloys.
North Texas University, Ordering in Antimonide Alloys

Recognitions, Honors and Awards (at least partly attributable to support under this FWP):
Our paper on "Amphoteric Refractions" was cited as one of the Top 15 Physics Stories of 2003 as well as cited in Physics Today, 2003. Over 114 Physical Review publications and over 15 Physical Review Letters on the subject of Spontaneous Ordering, Over 29 Invited Talks.

Personnel Commitments for FY2007 to Nearest +/- 10%:
B. Fluegel (35%), Y. Zhang (50%), W. McMahon (50%), Mascarenhas 30% .

Authorized Budget (BA) for FY05, FY06, FY07:
FY05 $609,000 **FY06 BA $597,000** **FY07 BA $597,000**

Laboratory Name: National Renewable Energy Lab
B&R Code: KC020202

FWP and possible subtask under FWP:
Physics of Isoelectronic Co-doping

FWP Number:
ERWER2B

Program Scope:
Isoelectronic co-doping GaAs and GaP with Bismuth and Nitrogen is proposed as a novel method for regularizing the abnormal alloy behavior that is observed in these materials when they are doped with Nitrogen alone. The technique will lead to enhancements in 1) the solubility of isoelectronic dopants, and 2) carrier mobilities as compared to doping with Nitrogen alone. The use of the technique will make it possible in several situations to overcome the limitations imposed by semiconductor alloy constraints on the design of some technological important devices such as such as solar cells, lasers and LED's. Most importantly, it will enable the growth of photonic devices on Silicon substrates. The proposed research will advance the basic understanding of the Mott-transition in heavily doped semiconductors as well as help unravel the fundamental mechanisms of alloy formation.

Major Program Achievements (over duration of support):
First observation of Nitrogen resonant impurity level and of effective mass anomalies in GaAsN, of giant bandgap bowing in GaPN, and of the impurity band physics. Invention of the concept of isoelectronic co-doping for regularizing optoelectronic properties of GaAs:N and GaP:N. First successful incorporation of Bi into GaAs that showed isoelectronic trap like behavior. The technique of resonant light scattering for probing localized electronic states was pioneered under this project. The research has also led to the first identification of 1) spatially resolved impurity pairs in alloys 2) of giant spin-orbit bowing in semiconductors, and 3) of the potential use of dilute bismide alloys for plasmonics.

Program impact:
The research resulting from this project has set the trend for most of the current perspective of the mechanisms underlying the giant bandgap bowing in dilute Nitride Alloys. A patent with 165 claims for optoelectronic devices based on the invention of the concept of isoelectrnic co-doping has been awarded and the research has resulted in 53 publications (two Phys. Rev. Lett. and one Nature Photonics).

Interactions:
Univ. of Houston, Growth of GaAs:N
Univ. of British Columbia, Growth of GaAs:Bi
Univ. of Montreal, Rutherford Backscattering studies.
Sogang University (Seoul, Korea), LPE growth of GaAs:Bi:N, GaP:Bi:N
Sandia National Labs, Growth of GaAsN Quantum Wells.
National High Magnetic Field Lab., Florida State Univ., High Magnetic Field Studies
Institute of Semiconductors (Beijing), High Pressure studies.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Eight Invited Talks, 5 Invited Papers, 53 research publications (2 Phys. Rev Lett.), 1 patent, 2 book chapt.

Personnel Commitments for FY2007 to Nearest +/- 10%:
Y. Zhang(10%), 1.5 Postdoc, A. Mascarenhas (30%), B. Fluegel (30%)

Authorized Budget (BA) for FY05, FY06, FY07:
FY05 BA $320,000 **FY06 BA $363,000** **FY07 BA $390,000**

Laboratory Name: National Renewable Energy Lab
B&R Code: KC0202030

FWP and possible subtask under FWP:
Understanding Molecular Hydrogen Absorbents: A First Principles Theory for van der Waals Interactions

FWP Number:
ER21

Program Scope:
(i) To develop effective and efficient first-principles approaches to the study of van der Waals (vdW) interactions between molecular hydrogen and realistic molecular-hydrogen absorbents and (ii) to provide the fundamental knowledge for meeting the grand challenge of developing a secure, compact, lightweight, and economic method of storing hydrogen fuel onboard vehicles.

Major Program Achievements (over duration of support):
Our project started at the end of August 2006. In the last 14 months, we have made breakthroughs in developing a local atom-centered potential approach to successfully reproduce the vdW interactions in a range of vdW systems from inert gas molecules to H_2 interaction with graphitic carbon molecules. As it stands now, the computational time remains at that of standard density functional calculations, while the accuracy is approaching that of state-of-the-art coupled cluster quantum chemistry calculations. From these studies, we are able to determine the general potential form with respect to the separation between molecules. Meanwhile, we worked on practical weak-interaction hydrogen adsorbents. Our work on H_2 adsorption on metal organic frameworks (MOFs) solved the recent experimental puzzle why exposed metal sites enhance H_2 binding roughly by a fact of two than pure physisorption. We proposed a new molecular hydrogen adsorption system, i.e., nano-engineered calcium intercalated graphite in which the Ca is used to adsorb the H_2. We show that in such a system, the theoretical volumetric capacity can easily exceed that of liquid hydrogen, as well as the DOE 2015 target. Moreover, not only the gravimetric capacity is still at the level of DOE 2015 target, but also the tendency of metal clustering can be eliminated. Last but not least, we made breakthroughs in understanding hydrogen spillover in realistic MOF systems for room temperature hydrogen storage. New design strategies are been explored to improve the H uptake kinetics.

Program impact:
The work on H_2-MOF interaction was published in J Am Chem Soc. The paper on intercalated Ca has been submitted to Phys. Rev. Lett. We are also finishing up the papers on the atom-centered potential formalism and hydrogen spillover mechanism. The PI is organizing a 2008 Spring MRS Symposium on weak interaction scenario and the 2008 DOE Theory focus session on hydrogen storage materials. One MS&T invited talk on the MOF work. Y.-H. Kim is invited to talk on the atom-centered potential approach and D. West is invited to talk on accelerated molecular dynamics for spillover of hydrogen on graphene.

Interactions:
Eric Schwegler, Livermore National Laboratory

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

Personnel Commitments for FY2007 to Nearest +/- 10%:
Shengbai Zhang (Principal Investigator) 5%
Yong-Hyun Kim (co-PI) 40%
Yiyang Sun (post-doc) 100%
Kyuho Lee (post-doc) 100%
Damien West (post-doc) 5%

Authorized Budget (BA) for FY05, FY06, FY07:
FY06 BA $300,000 **FY07 BA $300,000**

Laboratory Name: National Renewable Energy Lab
B&R Code: KC0202030

FWP and possible subtask under FWP:
Million-Atom Nanostructure Architecture
FWP Number: ER5A.1000

Program Scope:
Whereas contemporary electronic structure theory is largely dealing with molecules, clusters and solids containing up to ~100 atoms in the computational cell, recent experimental advances now pose staggeringly more difficult challenges to theory and simulation efforts of nanostructures in three areas: (i) the need to address *large* single nanostructures, in the range of 10^3-10^6 atoms, (ii) the need to deal with the *complexity of the underlying electronic phenomena*, including quantum entanglement, excitonic complexes, exchange-induced fine-structure, Coulomb and spin blockades, and unusual decay mechanisms of excited states (e.g., multi exciton generation from one photon), and (iii) the emergence of *nanostructure systems*, involving combined *3D architectures* of quantum dots, wires and wells (0D, 1D, 2D, respectively), as the main vehicle for nano devices and nano technology. This project addresses such challenges as follows: (a) Develop an atomistic pseudopotential approach capable of addressing the single-particle problem of million-atom nanostructures; (b) Develop a many-body (configuration interaction) approach for the same nanostructures; (c) Study the complex nanoscience phenomenology of inter-band and intra-band optical spectra, quantum entanglement of the many-particle wave functions, multi-exciton complexes, Coulomb- and spin-blockade, and excited-state carrier relaxation, and explain the recent experimental observations in these areas, (d) Address complex nanostructure *systems* combining 0D, 1D and 2D building blocks, and (e) Offer design capabilities, via the "inverse band structure" approach, to predict the structure of systems that have prescribed electronic properties. **Vision for future:** Having invested in developing over the past few years the theoretical and computational tools needed to describe realistically complex nanostructures and complex phenomena therein, we are now moving to apply these methodologies to *research bottlenecks faced by nanostructure-based solar energy technologies*. Specifically (i) Basic studies into the mechanism of carrier-multiplication in quantum dots, (ii) Intermediate-band solar cell simulations, and (iii) Material screening for inorganic nanostructure solar cells. The co-location of this fundamental research effort within the applied groups at NREL promises mutual synergism.

Major Program Achievements (over duration of support):
(i) Development of new computational and theoretical approaches to items (a) and (b) above, (ii) the application of these new methodologies to most of the physical phenomena described under item (c) for self-assembled million-atom InAs/GaAs prototype nanostructures, (iii) the calculation of inter-band and intra-band absorption spectra, Coulomb blockade effects, fine-structure splittings, and carrier multiplication rates [item (c) above] in PbSe colloidal quantum dots containing a few thousand atoms, (iv) the study of radiative recombination lifetime, emission polarization, and multi-exciton emission spectra in CdSe colloidal quantum dots [item (c)], and (v) the prediction of electron localization and wave-function entanglement in complex, three-dimensional CdSe/CdTe nano dumbbells [item (d)]. Our cumulative work has formed the basis of the current theoretical understanding of large semiconductor quantum dots.

Program impact:
Theoretical explanation of the main physical effects observed spectroscopically in self-assembled quantum dots, including excitonic spectra and its dependence on size and shape; multi-exciton energies; exchange-splitting; excitonic fine-structure; intra-band transitions; effects of electric fields on dot; quantum entanglement in dot molecules; singlet-triplet splitting. For colloidal dots we explained Auger relaxation dynamics and mechanism of carrier-multiplication.

Interactions: This is a collaboration between NREL and LBNL, ORNL and U. of Tennessee
Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
In the 3 years since program started published 65 papers, including 8 in Phys Rev Letters, and delivered 18 Invited Talks, including 2 March Meeting Invited talks.
Personnel Commitments for FY2007 to Nearest +/- 10%:
A. Zunger (Lead-PI; 15 %); A.Franceschetti (20 %); G.Bester (100%); two post docs (100%)

Authorized Budget (BA) for FY05, FY06, FY07:
FY05 BA $585,000 **FY06 BA $575,000** **FY07 BA $575,000**

Laboratory Name: National Renewable Energy Lab
B&R Code: KC0202030

FWP and possible subtask under FWP:
Semiconductor Theory

FWP Number: ER62.0101

Program Scope:
Semiconductor-based energy technologies involve a rather complex mix of materials, phases and interfaces that are very hard to study and optimize experimentally. For example, photovoltaic solar cells, light-emitting diodes, solid-state lasers and solid-state lightning often require a few layers of different materials, surfaces and interfaces, random alloys, (partially) ordered alloys, as well as n- and p-type doping. Understanding of the operation of the system and optimizing it requires *disentangling the physical behavior of the components*, an endeavor that has historically proven to be experimentally very difficult, if not impossible. The role of the project is to develop a fundamental understanding of the semiconductor materials and *individual* underlying physical phenomena that control such semiconductor-based energy technologies, allowing better design and control. The physical phenomena we address are: (a) *Bulk physics*--the basic electronic structure, optical and mechanical properties of the crystalline building blocks of semiconductor material science. (b) *Surfaces and interfaces of semiconductors*--surface-induced ordering, interfacial interdiffusion and their effect on electronic properties. (c) *Defect physics of semiconductors*--the way that point-defects affect the electronic and transport properties. (d) *Dopability of semiconductors*--understanding what it takes to introduce electrons and holes into a material. (e) *Physics of semiconductor alloys*--optical bowing, short range order, clustering and phase-diagrams. **Vision for the future:** We are now applying the theoretical development in areas (a)-(e) above to (1) *Design solar-energy related materials via the Inverse Band Structure* approach--given a desired target property (defect engineering or band-gap engineering), find the atomic and crystal structure having this property, (2) Provide a "bridge" between alloy microstructure and its electronic properties. The co-location of this fundamental research effort within the applied groups at NREL promises mutual synergism.

Major Program Achievements (over duration of support):
We have developed novel theoretical techniques needed for the above research, including novel pseudo potentials approaches; new schemes for Exchange and Correlation; Mixed-Basis Cluster Expansion (MBCE) methods to study alloy phase stability; Inverse Band Structure (IBS) method to survey a large number of materials, searching for the one with prescribed properties. Current work includes: (1) theoretical explanation of defect structures in chalcogenides which impede their photovoltaic action; (2) first-principles prediction of alloy thermodynamic quantities (e.g., phase-diagrams, short range order) for epitaxial semiconductor alloys; (3) calculation of electronic properties of nitride InGaN alloys and transparent oxides (ZnO; In_2O_3); (4) prediction of properties of unusual ternary materials (e.g., ordered vacancy compounds); (5) physics of unusual superlattices (e.g., InAs/GaSb); and (6) properties resulting from combining semiconductivity with magnetism (e.g. (Ga, Mn) As).

Program impact:
Established a systematic and quantitative theoretical approach to predict novel alloy phases and their thermodynamic properties from first-principles calculations; developed the Inverse Band Structure approach for finding materials with designated properties; established basic theory of semiconductor alloy ordering and bowing.

Interactions:

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
A. Zunger: John Bardeen Award of TMS (2001); A. Rahman award of APS (2001); published over 120 papers in Phys Rev Letters and Rapid Communication; 23 Invited papers in leading conferences.

Personnel Commitments for FY2007 to Nearest +/- 10%:
A. Zunger (Lead-PI; 15 %); three post docs (100%).

Authorized Budget (BA) for FY05, FY06, FY07:
FY05 BA $350,000 **FY06 BA $340,000** **FY07 BA $340,000**

Laboratory Name: National Renewable Energy Lab
B&R Code: KC020301

FWP and possible subtask under FWP:
Carbon Nanotube Membranes and Adsorbents

FWP Number: ERWER0L

Program Scope:
Investigate basic science of nanotube membranes and materials in gas separation, sorption, and fuel cell science. Design boundary interfaces on the nanoscale. Explore electrocatalysis on nanotube-supported materials. Understand the adsorption, transport, and reactivity (gas phase and electrochemical) of molecules such as H_2, O_2, H_2O, CH_4, and CO_2 on the surfaces of carbon nanotube materials and membranes, and on carbon nanotube materials decorated with catalysts. Develop synthetic methods to produce desired doped and metal-decorated materials, electrodes and crystals.

Major Program Achievements (over duration of support):
Separated carbon single-wall nanotubes (SWNTs) according to conductivity type and formed transparent thin film electrodes. Observed significant differences in electrochemical charge storage capacity which can be attributed to differences in the Fermi levels of the nanotubes. Adsorbed species on thin films have been monitored by transmission using FTIR and Raman spectroscopies. Synthesized first boron-doped nanotubes by laser vaporization after discovery of novel catalyst. Determined p-type conductivity by ^{13}C nmr spectroscopy. Chemical vapor deposition growth of SWNTs near equilibrium was followed using Raman spectroscopy, permitting the first experimental determination of the Gibbs free energy of SWNT formation. A new synthetic method was developed which combines the best aspects of conventional laser and arc growth methods and offers high production rate of low-defect density nanotubes. Platinum-doped nanotubes synthesized by this method show improved activity as fuel cell electrodes. SWNT/polymer composite membranes offer dual transport pathways for improved performance over either material alone.

Program impact:
Advanced the understanding of transport and reactivity of important energy-related small molecules on nanotube surfaces, membranes, and electrodes. Developed methods to fabricate carbon nanotube membranes. Explored metal-decorated nanotube materials for use in catalysis and fuel cells. Measured the thermodynamics of single-wall carbon nanotube growth. Advanced nanotube growth science and technology.

Interactions:
Internal - OS/DMS Theory (S. Zhang); OS/DCS Nanoscience "Intermediating Quantum Dot communication with carbon nanotubes and proteins"; DOE Center of Excellence on Hydrogen Sorption Materials; DOE PV Program.
External - ORNL, LLNL, NIST, NASA, Rochester Institute of Technology, Rice U., U. of Quebec, U. of Michigan, Caltech, Stanford U., U. Pennsylvania, Penn State, North Carolina State University, Air Products and Chemical, Inc.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Heben – International Energy Agency expert on hydrogen storage; President's Hydrogen Technical Advisory Panel Year 2000 Research award; Lead of DOE/EERE Center of Excellence on Hydrogen Sorption; Organizer of symposia at: Fall 2004 MRS, Summer 2005 IPHE meeting, Spring 2006 MRS meeting, Summer 2006 ECS Meeting, Summer 2007 ECS Meeting. Invited speaker 2007 Purdue student Pugwash.
Dillon – Organizer Fall 2005 MRS meeting. NSF, MRSEC Review Panels. Plenary speaker honoring Claire Boothe Luce to promote women in science, 2003. National Academy of Engineering Symposium on *Frontiers of Engineering*, 2006. Keynote lecture at the 2005 Taiwan Symposium on Hydrogen Storage in Carbon Nanomaterials, Oct. 18, 2005 Taipei, Taiwan. Dillon/Heben ~ 36 invited talks since 2001.

Personnel Commitments for FY2007 to Nearest +/- 10%:
M.J. Heben – PI (10%); A.C. Dillon (10%); C. Engtrakul (50%); J. Blackburn (10%) .

Authorized Budget (BA) for FY05, FY06, FY07:
FY05 BA $215,000 **FY06 BA $215,000** **FY07 BA $215,000**