FWP Title: Electronic and Optical Processes in Novel Semiconductors for Energy Applications **National Renewable Energy Lab.**

FWP Number: ERW0523 **B&R Code: KC020103 & KC020202**

Program Abstract:

Advanced energy technologies require high-performance materials, which in photovoltaics and in solid-state lighting(SSL) translates to new materials to efficiently absorb sunlight, and to efficiently convert electricity to white light respectively. A goal of this project is fundamental materials research for the realization of semiconductors that transcend the existing limitations that constrain present photovoltaic and solid-state lighting technologies. It specifically addresses the current unavailability of efficient high bandgap (2.1 eV) emitters for SSL and low bandgap (1 eV) absorbers for photovoltaics,, via technologies based on GaAs substrates. The key to transcending the present limitations, is the understanding and control of fundamental electronic and optical processes in semiconductors, which is another goal of this project. Towards this, the project will focus on understanding the phenomena of spontaneous ordering in high bandgap lattice-mismatched $Ga_xIn_{1-x}P$, and the abnormal electronic structure and properties of isoelectronic dopants N and Bi in GaAs. Additionally, it will address recent observations of new excitations in bipolar plasmon gasses photogenerated in semiconductors, so as to achieve an understanding of collective phenomena that could enable semiconductors with novel, useful properties. Through collaborative efforts, this project utilizes state-of-the art resources in growth, spectroscopy, and theory, from three national laboratories, to address the above mentioned issues. By exploiting the use of BES Nanoscience Centers, and Supercomputer Facilities, it brings to bear new tools for the growth and characterization of semiconductors, and connects BES theory and computation programs with the experimental work in BES supported DOE Laboratory research.

Program Impact:

The issues that this project attempts to address are long-range fundamental research issues that if solved, will make it possible to leap-frog solar cells efficiencies from current peak values of 40% to values above 50%, and SSL white light-emitting diode wall-plug efficiencies from current values < 15% to values above 50%. This project benefits from the extensive expertise on the growth and characterization of lattice-mismatched $Ga_XIn_{1-x}P$ and dilute bismide alloys for solar cells, that presently exists at NREL's National Center for Photovoltaics, as well as from the extensive semiconductor growth, analytical and structural characterization equipment located in that center. The synergism in having this cross-center collaboration at NREL (between DOE/BES supported fundamental research and DOE/EERE supported applied research) led to much of the previous breakthroughs, in our earlier pioneering studies on spontaneous ordering in semiconductor alloys and on isolectronic doping in semiconductor alloys, as well as significantly impacted the development of the highest efficiency photovoltaic technologies at NREL.

FY 2009 Authorized Budget (New BA): $997k

Program Personnel Supported in FY2009:

Angelo Mascarenhas, PI: 60%, Brian Fluegel (Senior Scientist): 75% , Yong Zhang (Senior Scientist): 50%, Lekhnath Bhusal (postdoc): 100%, Rajeev Kini (postdoc): 100%

Interactions:

Collaborators: Loren Pfeiffer (Princeton), David Snoke (Pittsburgh), Center for Integrated Nanotechnologies (New Mexico), Eric Shaner (Sandia , Albuquerque), Gabor Kalman (Boston College), R.P.G. Karunasiri (Naval Postgraduate School), L. Wang (NERSC/LBNL), Tom Tiedje (Univ. of Victoria), Aaron Ptak (NREL/NCPV), Myles Steiner (NREL/NCPV)

Program Abstract:

This "Semiconductor Theory" project aims at creating the fundamental solid-state physics underpinning of energy-related semiconductors and nanostructures using state-of-the-art tools of condensed matter theory. 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 and light-emitting diodes 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 this project is to develop a fundamental understanding of the *basic mechanisms* underlying the generic building blocks of energy conversion. Current work focuses on two areas (i) forging an understanding of the relationships between *atomic microstructure in alloys* (clustering, phase-separation, nanostructure formation, etc) and its ensuing *electronic structure* (localization, charge separation, band gap bowing etc) and (ii) deciphering the basic mechanisms by which quantum dots can solve solar photo conversion problems that are difficult with other morphologies (e.g., thin-film) . This work is distinct from the EFRC on Inverse –Design (focusing on search and optimization of new materials via Inverse Band Structure) and from DOE technology office work (focusing on improvements in currently used solar conversion materials).

Program Impact:

Various deviations from perfect order or perfect randomness have been observed in alloys and compounds, including nanostructure formation as self-assembled dots, various forms of precipitates from solid-solutions, long and short-range ordering, clustering, and phase separation. Yet, most theoretical descriptions of electronic properties of matter (optical, magnetic, and thermodynamic) tacitly assume rather idealized atomic microstructures: perfect order in crystals or perfect randomness in solid solutions. Conversely, most theoretical descriptions of the atomic microstructure of matter do not predict the electronic properties that ensue from such atomic microstructures.

Yet, we know that atomic microstructures are rarely ideal. For example, the optical and transport properties of random alloys and ordered alloys of the same composition can be very different. The transport properties of carriers in different "polytypes" of SiC (same composition, different bond orientation) can differ dramatically, including the possibility of spatial electron-hole separation in some cases. The piezoelectric response and excitonic transitions of abrupt vs. interdiffused interfaces are rather different. In metallurgy, we know that precipitate can significantly affect strength, whereas in oxides, persistent off-stoichiometry (e.g., In_2O_3 or NiO) controls free-carrier densities. In semiconductor alloys, epitaxial morphology can enhance the equilibrium solid solubility, or lead to long-range ordering with its ensuing dramatic effect on carrier transport.

Furthermore, the advent of atomic-scale characterization methods (X-STM; high-resolution diffraction atom microprobes, high-resolution TEM, etc.) allows one to observe the microstructure that results from a <u>given</u> crystal growth protocol. The sequence of events in the pertinent <u>*experimental*</u> studies is thus: *Select growth protocol → Observe microstructure → Measure physical properties***.** The obvious "missing link" is the absence of reverse feedback: the above sequence of events does not tell you how to alter the growth protocol to affect a desired change in some material properties. On the other hand, the sequence of events in the pertinent <u>*theoretical*</u> studies is often: *Assume atomic structure/microstructure → Predict physical properties***.** The obvious "missing link" is the possible lack of realism in describing the microstructure (limiting the ability to make a compelling comparison with experiment) and the lack of reverse feedback (limiting the ability of real design).

The basic idea of this project is to build upon our previously developed capabilities of (i) prediction of *microstructure* from first-principles statistical simulations, and (ii) ability to perform large-scale *electronic structure* calculations of "supercells" having prescribed atomic microstructure. Considering precipitation of quantum dots in a matrix as a special microstructure, we will add (iii) the ability to predict the electronic structure of quantum dots from pseudopotential Configuration-Interaction (CI) calculations. Our position is that this is the moment in time for first-principles theorists to direct their talents towards a concerted and simultaneous description of atomic microstructures *and* the ensuing physical properties.

FY 2009 Authorized Budget (New BA): $340K

Program Personnel Supported in FY2009: A. Zunger (PI and FTE 20%), Jennifer Chan (post-Doc) ; V. Popescu (Post doc) ; X. Zhang (post Doc)

FWP Title: Hydroxide Conductors for Fuel Cells and Electrolyzers National Renewable Energy Laboratory
FWP Number: ERWER23 B&R Code: KC020301

Program Abstract: The vision of a Hydrogen Economy is compelling for reasons of improved energy security and environmental impact; however, before such a vision can be met there are major technological barriers that must be overcome. Namely, commercially viable technologies for the production (electrolyzers) and the use (fuel cells) of hydrogen must be developed. Hydroxide conducting systems can be used for either production or use of hydrogen and offer specific advantages compared to competing technology. To date, investigation of hydroxide conductors for fuel cells or electrolyzers has been limited due to perceived limitations of durability, conductivity and/or carbonate formation. Our program combines experts in the area of fuel cells, synthetic chemistry and modeling to elucidate decay mechanisms and design new chemical structures to overcome them. The primary advantage of hydroxide conductors is the enablement of non-precious metal catalysis, a critical showstopper to widespread implementation of traditional (acidic) fuel cells and a potential advantage for electrolyzers. We have used chemical and thermal degradation studies of target cations for use in anion exchange membranes (AEMs) to elucidate the degradation mechanisms and rates of target cations and correlated these studies with computational studies. These studies have shown the unexpected importance of ylide formation as a degradation pathway, the role of water (solvating media) in stabilizing cations, and have explored cations with increased stability. While membranes using the standard tetraalkyl ammonium cations have been reported to show poor stability at even 60C, we have found that representative cations of these membranes show reasonable stability at much higher temperatures when sufficiently high water contents are present. Recent advances in AEM durability have been reported that are in reasonable agreement with our experimental studies of cation durability, suggesting current AEMs may have the durability required for some limited applications. A specific cation featuring an ether linkage showed approximately 4x improved durability in accelerated testing. We have begun studies involving carbonate and bicarbonate in these systems as these species will be present whenever carbon dioxide is present and appear to be a potential limiting factor in the performance of AEMs.

Program Impact: The work has led to significant advances in the field, improving quantification of cation stability and showing AEM based devices can have durability requisite for specific commercial applications. We have shown three, specific cations have improved base stability compared to the standard benzyl trimethyl ammonium cation typical used in AEMs. We have identified cation decomposition mechanisms that have been underappreciated for these materials. This knowledge will be used to guide the design of anion exchange membranes in the future. There has been significantly increased effort by the research community being placed toward anion exchange membranes since this project was initially funded, and this project has played a meaningful role in stimulating this increased interest. For example, a workshop chaired and organized by the project PI has led to an Army Research Office Multi University Research Initiative Request for Proposals that is currently in the review stage.

FY 2009 Authorized Budget (New BA): $270K

Program Personnel Supported in FY2009 to Nearest +/- 10% FTE
Bryan Pivovar (PI) 20%, Hai Long 30% and Chaiwat Engtrakul 10% (Technical Support Staff).

Interactions: (limit to current interactions and collaborations)
This project began at Los Alamos National Laboratory (LANL). The PI for the project joined NREL but maintained interactions with Jim Boncella and Shaji Chempath at LANL. Collaborations with Cellera, Inc., Diahatsu, Colorado School of Mines, Penn State University and University of California-Riverside.