

Predict the optical, electrical, and thermal properties of semiconductors containing impurities and defects using first-principles theory. Most of the research involves crystalline silicon, but diamond, GaN and other semiconductors are of interest as well. The calculations include static properties (stable and metastable configurations, energetics, electronic structures, charge and spin states, gap levels), classical molecular-dynamics simulations (diffusion, reactions, etc.), vibrational dynamics (vibrational spectra, vibrational lifetimes and decay processes), as well as $T > 0K$ dynamics (free energies, thermal conductivities).

Defects determine many of the mechanical, electrical, optical and maybe thermal properties of semiconductors. Oxygen and nitrogen impurities strengthen crystalline Si by locking dislocation. The type and concentration of charge carriers are controlled by dopants. The charge carrier lifetimes are determined by the presence of native defects and deep-level impurities such as transition metals. Hydrogen passivates the electrical activity of many defect centers.

Light impurities almost always give rise to local vibrational modes which can be observed by infrared or Raman spectroscopy. Sharp photoluminescence bands often characterize specific defect centers. In some case, phonon sidebands indicate the presence of low-frequency pseudolocal modes. The various defects and impurities interact with each other at finite temperatures. The diffusion of many impurities, including dopants, is strongly affected by native defects. Trace amounts of transition metal impurities, such as Fe, can cause metal-oxide-semiconductor transistors to leak. Thus, understanding the physics and chemistry of defects in semiconductors has substantial relevance.

The interplay between theory and experiment has proved to be a most powerful tool to unravel the sometimes unexpected behavior of defects. This is why I collaborate with experimentalists in the field as often as possible.

My interests deal with the properties of a wide range of defects, mostly in crystalline silicon, but my group has done work on c-C, Ge, and GaN as well. All our calculations are of the 'first principles' type, which means that none of the parameters are fitted to measured quantities.

In these calculations, the host crystals are represented by periodic supercells ranging in size from 64 to 216 (and larger) host atoms. The k-point sampling is a $2 \times 2 \times 2$ or $3 \times 3 \times 3$ Monkhorst-Pack mesh for the energetics and the calculation of gap levels but the dynamical matrices are normally calculated with $k=0$. The phonon densities of state are obtained using 90 or more k points. The electronic problem is solved using self-consistent density-functional theory, within the local or general gradient density approximations. Ab-initio type pseudopotentials are used to remove the core regions from the calculations. The basis sets for the valence states consist of (numerical) atomic-like orbitals of the Sankey type. Double-zeta basis sets, with or without polarization functions, are the norm. These calculations are done within the SIESTA code. We also use the plane-wave VASP software package when dealing with transition metal impurities.

Static ($T=0K$) calculations begin with geometry optimizations using conjugate gradients (or simulated quenching). These are converged until the largest force component is $0.005eV/\text{\AA}$ or less. The formation and/or binding energies are calculated and the charge and/or spin distribution can be extracted. Multiple k-point calculations provide insight into the electronic structure of the defect in the

stable (or metastable) states. Outputs include a wealth of chemical details: overlap populations Mulliken charge distributions, etc. The gap levels of the defect are estimated using the ‘marker method’ developed at the University of Exeter.

Defect diffusion and reactions are obtained from classical molecular-dynamics (MD) simulations. The temperature of the cell is set by the kinetic energy of the ions, which are treated like classical particles. At a given time t , the total energy (electronic + nuclear) allows the calculation of classical forces on each nucleus, and Newton's law of motion is used to compute the velocity and position of each nucleus at a later time $t+\Delta t$, with Δt of the order of one femtosecond. Each nucleus is moved to its new position and assigned its new velocity, and the calculation begins again from scratch. The initial conditions (positions and velocities at $t = 0$) are set in such a way that the system is in thermal equilibrium without the need for thermalization (or a thermostat).

The dynamic matrices are calculated at T=0K using linear response theory or the direct ‘frozen-phonon’ approach. The eigenvalues of this matrix are all the normal-mode frequencies of the cell, including the local modes of light impurities, the resonant modes associated with strained host-atom bonds, and the phonon frequencies. The dynamical matrix can be evaluated at many k-points in the Brillouin zone of the supercell, thus allowing the calculation of high-quality phonon densities of state. The eigenvectors of this matrix can be used to determine the symmetry of specific modes and quantify their localization. This allows the identification of pseudolocal modes and sometimes of phonon replicas in photoluminescence bands.

The knowledge of the eigenvectors of the dynamical matrix also allows us to ‘prepare’ a supercell in a specific vibrational eigenstate. Constant-temperature simulations can then be performed to monitor the lifetime and decay of that normal mode. Carefully prepared supercells at different temperatures can also be used to investigate the thermal conductivity of the material.

The knowledge of the phonon density of states also allows the calculation of the Helmholtz free energy. From it, one can obtain total zero-point energies, vibrational entropies, and specific heats (at constant volume). If the other contributions to the free energy are included (rotational, electronic, or configurational), then the energetics of defects can be calculated vs. T from first principles.

RESEARCH SUPPORT

6/09-5/12: **Robert A. Welch Foundation, \$210,000 (pending)**

Dynamics of Impurities in Semiconductors

1/09-12/11: **BP Solar, \$238,746 (pending)**

Defect and Impurity Engineering for Crystalline Silicon Solar Cells

6/06-5/09: **Robert A. Welch Foundation, \$180,000**

Dynamics of Impurities and Defects in Semiconductors

10/07-9/09: **Silicon Solar Consortium, \$45,250**

Microscopic Studies of Recombination Centers, Passivation, and Hydrogenation

3/05-9/05: **National Renewable Energy Laboratory, \$73,072 (50% with Lehigh University):**

extension: *Hydrogenation Methods and Passivation Mechanisms in crystalline Silicon Photovoltaics*

6/03-5/06: **Robert A. Welch Foundation, \$160,000**

Dynamics of Defects in Silicon

10/01-3/05: **National Renewable Energy Laboratory, \$447,628** (50% with Lehigh University):

Hydrogenation Methods and Passivation Mechanisms in crystalline Silicon Photovoltaics

6/00-5/03: **Robert A. Welch Foundation, \$145,000**

Defect Reactions in Silicon

01/00-10/03: **National Renewable Energy Laboratory, \$109,405**

Research in Hydrogen Passivation of Defects and Impurities in Silicon

6/98-5/99: **National Renewable Energy Laboratory, \$44,998**

Theoretical Analysis of Hydrogen Passivation of Impurities and Defects in Silicon

6/97 -- 5/00: **Robert A. Welch Foundation, \$125,000**

Defect Reactions in Silicon

6/97-5/98: **National Renewable Energy Laboratory, \$44,983**

Theoretical Analysis of Hydrogen Passivation of Impurities and Defects in Silicon

1/97-12/97: **Swiss Center for Scientific Computing** (120 hours of supercomputer time):

Very Large-Scale Electronic Structure Calculations

2/96-2/97: **National Renewable Energy Laboratory, \$26,998**

Theoretical Analysis of Hydrogen-Vacancy-Impurity Complex Formation and Dissociation

1/96-12/96: **Swiss Center for Scientific Computing** (120 hours of supercomputer time):

Very Large-Scale Electronic Structure Calculations

6/95-12/95: **National Renewable Energy Laboratory, \$17,001**

Theoretical Analysis of Hydrogen-Vacancy Complex Formation and Diffusion in Silicon

1/95-12/95: **Swiss Center for Scientific Computing** (100 hours of supercomputer time):

Very Large-Scale Electronic Structure Calculations

6/94 -- 5/97: **Robert A. Welch Foundation, \$100,000**

Impurity and Defect Aggregates in Semiconductors

1/94-12/94: **Swiss Center for Scientific Computing** (90 hours of supercomputer time):

Very Large-Scale Electronic Structure Calculations

4/94-3/95: **National Renewable Energy Laboratory, \$24,992**

Theoretical Analysis of Hydrogen-Vacancy Complex Formation and Diffusion in Silicon

2/93-1/94: **National Renewable Energy Laboratory, \$29,709**

Theoretical Analysis of Hydrogen-Vacancy Complex Formation and Diffusion in Silicon

6/91 -- 5/94: **Robert A. Welch Foundation, \$91,000**

Hydrogen interactions in semiconductors

8/90: **Texas Tech University, \$20,975**

IBM RS6000/320 workstation

1/90 -- 12/91: **Advanced Technology Program** (State of Texas), **\$21,962**
Advanced molecular modeling software for quantum biochemical applications

6/88 --5/91: **Robert A. Welch Foundation, \$80,000**
Cluster modeling of semiconductors: the unusual bondings of boron in silicon

9/88 -- 8/89: **Institute for University Research, \$4,000**
Cluster modeling of semiconductors and applications

9/87 -- 8/88: **Institute for University Research, \$1,500**
Bond-centered interstitials in crystalline silicon

9/86: *Start-up funds*, Texas Tech University, **\$25,000**

6/86 -- 5/87: **Research Corporation, \$5,000**
Isolated hydrogen defect centers in diamond and silicon

9/85 -- 8/86: **Office of Advanced Studies and Research** (Rice University), **\$5,000**
Hydrogen-like interstitials in semiconductors

CURRENT AND FORMER STUDENTS IN MY GROUP

Charlie H. CHU: MS thesis 1989, left Texas Tech in December, 1990.

Mark A. ROBERSON: Ph.D. 1993, postdoc until 6/1995, now instructor at Vernon College.

Young PARK: postdoc in 1994, then staff member, Korean Institute of Technology (Seoul).

Jeffrey HASTINGS: MS, 2000, now MD (Inst. for Exercise and Environmental Medicine, Dallas)

Chuguang HE: graduate student 1996 - 1997, non-thesis MS degree, switched to Computer Science.

Maen GHARAIBEH: Ph.D., 2002, faculty member, Jordanian University of Science & Technology.

Kirby WELLS: undergraduate research in 1999, started MS research, now in industry.

Jason McAFEE: MS, 2004, now a Ph.D. student in chemistry.

Damien WEST: MS, 2003, Ph.D., 2007, now postdoc at Rensselaer Polytechnic Institute

Mahdi SANATI: postdoc 2002 to 2004, now a faculty member at Texas Tech.

Nevill GONZALEZ SZWACKI: postdoc, 2006 – 2008

Michael GIBBONS: Ph.D. student

Daniel BACKLUND: Ph.D. student