

We use first-principles theory to study a wide range of properties of defects in semiconductors, primarily crystalline Si and Si nanostructures. ‘First-principles’ refers to (i) periodic supercells to represent the host material, (ii) classical molecular-dynamics (MD) simulations for nuclear motion, (iii) *ab-initio* type pseudopotentials for the electronic core regions, and (iv) (spin) density-functional theory for the electronic valence regions. These basic tools are well suited to predict defect geometries, electrically-active levels in the gap (marker method), charge and spin states, migration paths and activation energies (nudged-elastic-band), local vibrational modes (LVMs), binding energies to common defects and impurities such as vacancies, self-interstitials, hydrogen, oxygen, dopants, etc.

In recent years, we have focused on the vibrational properties of defects and of the host crystal. This started with a series of unexpected vibrational-lifetime data obtained from transient-bleaching spectroscopy. The measured lifetimes of apparently similar Si-H stretch modes were observed to differ sometimes by as much as two orders of magnitude. Further, the observed isotope effects were often unexpectedly large. In order to calculate vibrational lifetimes as a function of temperature, we developed a new way to perform MD simulations – now known as ‘supercell preparation’. No thermostat is used and the temperature fluctuations are so small that we can monitor the energy and amplitude of all the normal vibrational modes in the system starting with MD step 1. Supercell preparation, papers, and scripts are available at <http://jupiter.phys.ttu.edu/stefanke/microcanonicalMD>.

The explanation of the experimental data related to the decay of excited oscillators involve the *receiving* modes. They determine the order of the decay (two-, three-, and sometimes four-phonon processes) and the vibrational lifetime. For example, a change of isotope which does not affect much the frequency of the excited mode may affect that of a receiving mode, thus causing a two-phonon decay to become a three-phonon decay.

We then applied the supercell preparation tool to calculate the thermal conductivity of Si nanostructures containing defects. The central result of these studies is that defects do not scatter thermal phonons as is commonly assumed. Instead, they trap phonons in localized defect-related modes for dozens, sometimes hundreds, of periods of oscillation. This is the fundamental reason why defects reduce heat flow: they trap small amounts of heat for meaningful lengths of time in defect-related modes. This trapping does not conserve momentum. Defects are not static scattering centers. Their dynamics play a central role.

These effects are particularly important when the defect is the interface between two materials, as occurs at surfaces, heterojunctions,  $\delta$ -layers, buried oxides, superlattices, etc. Our current research effort focuses on heat flow at such interfaces. The model host material is a 1D-periodic Si nanowire (~250 Si atoms) containing a 4 to 6 atomic-layer thick  $\delta$ -layers of C, Ge, or SiO<sub>x</sub>. In order to optimize the geometries and allow the layer to relax, we place this nanowire in a large 1D-periodic box.

The nanowire is prepared at the temperature  $T_{\text{cold}}$  and a thin layer at one end of the nanowire is prepared at a higher temperature  $T_{\text{hot}}$ . In order to force the heat to flow in a single direction and to avoid contamination from image hot slices in adjacent cells, we designed a periodic *cluster* by making the box longer than the nanowire: adjacent nanowires are separated by 22Å of vacuum. All the dangling bonds at the surface of the nanowire are H-saturated. The interactions between thermal phonons and defects can be summarized as follows.

1. Defects introduce new normal vibrational modes into the phonon density of states of the material. These new modes are localized in space: we call them **Spatially-Localized Modes (SLMs)**. Only a small number of atoms in the vicinity of the defect are involved in the oscillations. A subset of SLMs are the well-known high-frequency local-vibrational modes often seen in IR or Raman spectra. Low-frequency SLMs are sometimes visible as phonon sidebands in photoluminescence bands such as those often associated with transition-metal impurities in Si. The localization of SLMs can be

theoretically quantified using the eigenvectors of the dynamical matrix. The degree of localization varies but SLMs are associated with all the defects we have studied: point defects, small aggregates, surfaces, and interfaces.

2. A fundamental characteristic of SLMs is that, once excited above the background temperature, their **vibrational lifetime** is much longer than that of bulk modes – even those of very similar frequency. Vibrational lifetimes are measured and calculated in ps. However, it is not very useful to think of them in this unit. Indeed, our notion of time originates from the rotation of the Earth, which defines the length of one day. For non-scientific reasons, the day is divided into 24 hours, the hour into 60 minutes, the minute into 60 seconds, and shorter lengths of time suddenly become decimal, such as the ps. Thus, the second is an arbitrary length of time, even when defined in terms of atomic transitions. But a quantum oscillator in a solid is not concerned about the rotation of the Earth. Its unit of time is the period of oscillation. An event occurring within one period is ‘short’, while a length of time involving many periods of oscillation is ‘long’ – regardless of the actual number of picoseconds involved. We have calculated the lifetimes of many bulk and localized (defect-related) modes. A phonon in a bulk mode (above the background temperature) typically decays within a fraction of one period (fast) while a phonon in a SLM survives for dozens and sometimes hundreds of periods (very slow). Localized modes do not couple well to delocalized modes.

3. The interactions between thermal phonons and defects involve only the coupling between delocalized (bulk) and localized (defect-related) oscillators. No scattering process is involved. When SLMs exist in the temperature range  $T_{\text{background}} - T_{\text{heat front}}$ , then they are thermally excited within a few tenths of a ps (resonant excitation, a one-phonon process). If the SLMs are higher in frequency, then two- (or even three-) phonon processes are required and the defect stays at the background temperature for a much longer time. These SLM excitations typically survive for dozens of periods of oscillation before decaying into bulk modes.

### Heat flow at an interface

When we set up a T gradient in a Si nanowire containing a  $\delta$  layer of C, Ge, or  $\text{SiO}_x$ , heat propagates from the hot slice toward the interface and reaches it with the temperature  $T_{\text{hf}}$  (heat front temperature), which is higher than the interface temperature  $T_{\text{cold}}$ . The first step depends on the number and localization of interface SLMs in the frequency range  $\delta\omega = k_{\text{B}}T_{\text{hf}}/\hbar - k_{\text{B}}T_{\text{cold}}/\hbar$ .

If there are SLMs in the frequency range  $\delta\omega$ , they are resonantly excited by the thermal phonons in the same frequency range. This one-phonon process occurs on the sub-ps time scale and the interface temperature increases rapidly. The interface remains hot for the vibrational lifetime of the excited SLMs, and then the excitations decay into receiving thermal phonons on either side of the interface. For example, in the case of a Si/Ge interface with  $T_{\text{cold}} = 120\text{K}$  and  $T_{\text{hf}} = 150\text{K}$ , the excited SLMs will mostly decay on the Ge side because the heavy Ge has many more low-frequency receiving modes than Si. In this case and at this temperature, the effective coefficient on thermal transmission is large.

If there are no SLMs in the frequency range  $\delta\omega$ , then the interface (and the  $\delta$  layer) will remain cold until two-phonon processes ( $\sim 10$  ps) excite higher frequency SLMs and then, the interface traps heat. For example, in the case of a Si/C interface with  $T_{\text{cold}} = 120\text{K}$  and  $T_{\text{hf}} = 150\text{K}$ , the interface and the C layer remain cold for a long period of time, as heat remains trapped on the Si side. But in the temperature range 280 – 310K, interface SLMs are present, resonant excitations do occur, and the interface picks up energy within a fraction of a ps. Thus, the same interface behaves very differently in different temperature ranges.

Three factors are at play: First, the number, frequency, and localization of the SLMs associated with the interface; second, the temperature (background  $T_{\text{cold}}$  and heat front  $T_{\text{hf}}$ ); third, the number of receiving modes on either side of the interface in the appropriate frequency range. The latter depends on the phonon densities of state of the materials on both sides of the interface.

## Ongoing research

T.M. Gibbons and D.J. Backlund are calculating the properties of 3d transition-metal impurities in Si; M.B. Bebek and C.M. Stanley study the propagation of heat in nanostructures containing  $\delta$ -doped layers of C, Ge, or Si<sub>x</sub>. I have ongoing collaborations with groups at MIT, in Oslo, and Milano.

## External Collaborations

I have benefitted from collaborations over the years, with both theorists and experimentalists: Manuel Cardona (isotope effects on the specific heat and Debye temperature of C, Si, Ge, and GaN), Gordon Davies (isotope effects on the vibrational lifetimes of O-related modes in Si); Mike Stavola (hydrogen passivation in Si photovoltaics, isotope effects on vibrational lifetimes, carbon-hydrogen complexes in Si, and phonon trapping at defects); Len Feldman (temperature dependence of vibrational lifetimes); Sam Myers (thermal properties of the N vacancy at high T); Alexandra Carvalho (B-O defects in Si and Cu-related photoluminescence defects); Christian Carbogno and Matthias Scheffler (migration barriers for impurities in Si and thermal conductivities in Si nanostructures containing defects); Tonio Buonassisi (transition-metal impurities in Si).

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*Defect identification and mitigation in high-lifetime silicon materials: growth, processing, reliability*

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*Microscopic Studies of Recombination Centers, Passivation, and Hydrogenation*

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*Theoretical Analysis of Hydrogen Passivation of Impurities and Defects in Silicon*

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

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*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 Aggregates in Semiconductors*

1/94-12/94: **Swiss Center for Scientific Computing** (90 hours of supercomputer time):  
*Very Large-Scale Electronic Structure Calculations*

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

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

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*Hydrogen-like interstitials in semiconductors*

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