Quantum Design of Complex Nanostructured Electronic Materials

Andrew Williamson*

*Quantum Simulation Group
Lawrence Livermore National Laboratory
Livermore, CA 94550
williamson10@llnl.gov

ABSTRACT

In this paper we present the results of three projects designed to engineer novel, nanostructured materials with tailored electronic properties. (i) We describe the design of a silicon/germanium nanowire based thermoelectric material whose performance is enhanced by suppressing thermal transport and enhancing electronic transport. (ii) We describe the design of a silicon-based laser, constructed from silicon nanocrystals embedded in an amorphous silicon nitride matrix. (iii) We describe the use of first principles models to predict the optical response of silicon nanowires. These predictions are used to interpret the results of optical scatterometry metrology, which can measure the size, and surface roughness of nanoscale electronic devices produced by a combination of lithography and etching.

Keywords: first-principles simulation, density functional theory, electronic transport, thermoelectric materials.

1 INTRODUCTION

Over the last decade, our ability to predict the fundamental properties of nanoscale building blocks such as quantum dots, wires, and slabs has improved dramatically. In particular, first principles modeling techniques can now routinely predict how the structural, electronic, optical, and transport properties of these building blocks depends on their size, shape, composition, and surface structure.

In this paper we present the results of three projects designed to build upon these fundamental studies to engineer novel, nanostructured materials with tailored electronic properties. These complex, nanoscale heterostructure materials utilize both the unique properties of their nanoscale building blocks and the interactions between the constituent building blocks to engineer the ideal material properties. (i) We will describe the design of a silicon/germanium nanowire based thermoelectric material whose performance is enhanced by suppressing thermal transport and enhancing electronic transport. This is achieved by engineering the nanoscale confinement and scattering of phonons and electrons.

(ii) We will describe the design of a silicon based laser, constructed from silicon nanocrystals embedded in an amorphous silicon nitride matrix. Models of the electronic states in the nanocrystal, the surrounding matrix, and the interface between the two, enable us to optimize the optical efficiency of the emission and electrically pump the laser.

(iii) We will describe the use of first principles models to predict the optical response of silicon nanowires. These predictions are used to interpret the results of optical scatterometry metrology which can measure the size and surface roughness of nanoscale electronic devices produced by a combination of lithography and etching.

2 NANOSTRUCTURED THERMOELECTRIC MATERIALS

Recent progress in nanomaterials synthesis techniques has enabled the growth of semiconducting nanowires (NWs) with a range of sizes, growth directions, and surface structures. NWs are one-dimensional nanostructures that exhibit quantum confinement effects such as a strong size dependence of their electronic and optical properties. The ability to tune their opto-electronic properties makes NWs attractive candidates for a variety of applications such as photovoltaic materials, photodetectors, field-effect transistors inverters, light-emitting diodes and nano-scale sensors.

Among these many potential applications, recent studies have also shown that NWs demonstrate particular promise for fabricating thermoelectric (TE) materials. The suitability of a material for TE applications is characterized by its figure of merit ZT:

$$ZT = \frac{\sigma S^2 T}{\kappa_e + \kappa_i}$$

where S is the Seebeck coefficient, σ is the electronic conductivity, and κ_e and κ_i are the electronic and ionic contributions to the thermal conductivity. The electronic conductivity is proportional to the electronic mobility, which is inversely proportional to the electron mass. The electronic contribution to the thermal conductivity depends on both the electron mobility and the band energy of the electrons. The lattice conductivity depends on the phonon density of states and phonon scattering rates.

For five decades, many new materials have been investigated in the search for a higher TE figure of merit, but *ZT* remained stuck in the range of 0-1.[1] However, recent experimental studies have suggested that the value of *ZT* can be significantly increased by incorporating

nanostructures into the TE material. In these nanostructured TE materials, it has been proposed that quantum confinement provides a mechanism for engineering the electronic band structure to reduce the electron and hole masses, thereby increasing their mobilities and increasing σ. Additionally, the reduced size of nanostructures increases their surface to volume ratio, increasing the surface scattering of phonons, thus decreasing thermal conductivity and further increasing the TE figure of merit. However, it is not immediately obvious that introducing nanostructure into a TE will always increase the TE figure of merit. Any beneficial increase in the electrical conductivity produced by quantum confinement will also introduce a counteracting increase in the electronic contribution to the thermal conductivity. Also, while an increased surface to volume ratio will increase the surface scattering of phonons and reduce thermal conductivity, it will also increase the surface scattering of electrons, reducing σ. Therefore, predicting the effect of introducing nanostructure into a TE material requires quantitative first-principles calculations.

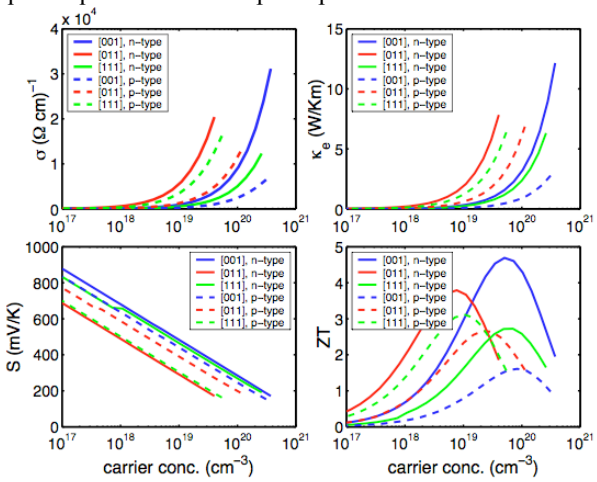

Figure 1: Calculated σ, κ_e, S, and ZT of p-type (dashed lines) and n type (solid lines) doped1.1nm SiNWs grown along the [001], [011], and[111] directions.

Figure 1 shows the calculated electronic conductivity, electronic contribution to thermal conductivity, Seebeck coefficient, and thermoelectric figure of merit, *ZT*, as a function carrier concentration for p- and n-type 1.1 nm SiNWs with different growth directions at 300K. In the calculation of *ZT*, the lattice contribution to the thermal conductivity is taken to be 1.9 W/Km. This value is computed data by Mingo *et al.*[2] The carrier concentration, *n*, is from the electronic density of states. In this model, *n* represents the concentration of charge carriers in a system that is artificially doped by varying the chemical potential while assuming a fixed band structure.

Figure 1 shows that as the concentration of electrons or holes increases, both the electronic conductivity and the electronic contribution to thermal conductivity increase as more carriers are available to transport both charge and heat, while the Seebeck coefficient decreases with increasing carrier concentration. In addition to a dependence on carrier concentration, all the properties also show a strong dependence on growth direction. This dependence arises from differences in the band structures of the SiNWs. For SiNWs grown in the [011] direction, the conduction band minimum (CBM) is highly dispersed, and the electronic states are delocalized in the direction parallel to the SiNW axis. In contrast, the CBMs in the [001] and [111] SiNWs are oriented in the direction diagonal and perpendicular to the NW axis, respectively, and their band structures are much flatter (see Reference [3]). Consequently, the [011] SiNWs have the lowest effective mass and highest conductivities for a given carrier concentration. Therefore, if one is only interested in selecting SiNWs with the highest electrical conductivity, these simulations predict that SiNWs grown in the [011] direction are the most promising.

However, for thermoelectric materials, the challenge is not simply to maximize the electrical conductivity, but to engineer an electronic band structure that maximizes the TE figure of merit. Figure 1 shows that *ZT* initially increases with carrier concentration as σ increases. At higher carrier concentrations, there is a net decrease of *ZT*. Therefore, for a given growth direction and type of doping, there is an optimal carrier concentration which yields the maximum attainable value of *ZT*. For the 1.1 nm wires shown in Figure 1, these optimal carrier concentrations vary between 10^{18} and 10^{20} cm^{-3}, producing maximum *ZT* values ranging from 1.5 to 4.6.

These are considerably higher than have been obtained for conventional thermoelectric materials and demonstrate the promise of using nanostructured materials for manufacturing thermoelectric materials with enhanced figures of merit.

3 SILICON NANOSTRUCTURES EMBEDDED IN SILICON NITRIDE

Light emission from silicon, to date the undisputed material in the microelectronics market, originates from low probability phonon-mediated transitions that unfavorably compete with fast, non-radiative de-excitation paths. The lack of practical silicon light emission severely limits the feasibility of monolithically integrated silicon optoelectronics that aim to combine electronic and optical functions on inexpensive integrated chips. However, several strategies have been recently developed to turn silicon into an efficient light-emitting material. The traditional approach is to reduce the dimensionality to nanometer scales, where both quantum confinement and surface chemistry effects improve the efficiency of light generation. Several groups have demonstrated light emission from silicon nanostructures embedded in SiO_2. However, embedding silicon nanoclusters in SiO_2 matrices prevents the fabrication of stable and efficient electrically-driven devices due to a huge barrier mismatch between silicon and SiO_2. Moreover, the achievement of high

NSTI-Nanotech 2007, www.nsti.org, ISBN 1420061828 Vol. 1, 2007

emission efficiency is severely impeded by the slow radiative lifetime (approx. 10 to 100 μs) which competes with much faster non-radiative channels such as Auger recombination. Therefore, there is a need to investigate alternative CMOS-compatible approaches that can yield intense and fast light emission in nanostructured silicon systems that are also suitable for efficient electrical excitation. An intriguing possibility is the nucleation of silicon nanoclusters in dielectric environments with smaller band-gaps than SiO_2. Tunable room temperature, visible light emission from silicon nanoclusters embedded in silicon nitride matrices with efficient electroluminescence have been recently demonstrated.

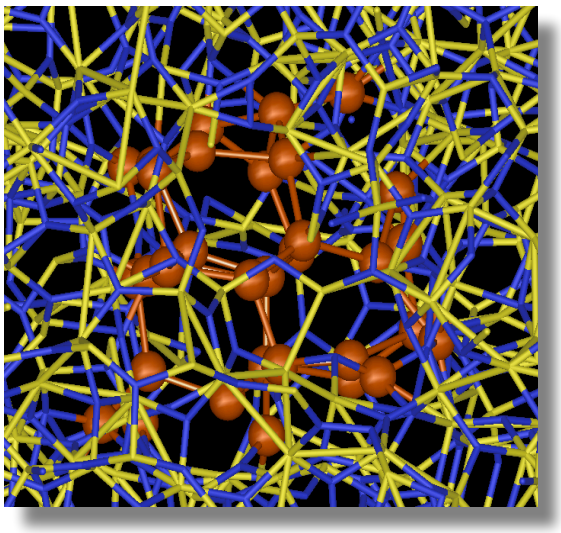

Figure 2: Structural model of a silicon nanoparticle embedded in amorphous silicon nitride.

Figure 2 shows a structural model of such a silicon nanocluster embedded in an amorphous silicon nitride matrix. Using this model, we analyzed the nature of the interface between the silicon nanocluster and the surrounding matrix. The different silicon-nitrogen groups existing at that interface were examined to see which are responsible for the light emission in the system. Figure 3 show structural motifs of each of these different surfaces groups. By calculating the optical gap and radiative lifetime of each of the prototype structures shown in Fig.3 we were able to identify those structures which most closely reproduced the optical properties measured by photoluminescence spectroscopy.[4] We find that structure f, which has a nitrogen atom bridged across the surface and connected to two silicon atoms has a calculated gap of 2.3 eV and a lifetime of 10 ns, which are in close agreement to the measured values of 2 eV and 10 ns.[4]

Additional simulations are being performed on the entire structural model shown in Fig.2 to confirm that the optical gaps predicted by the small prototype structures shown in Fig.3 are reproduced in larger systems.

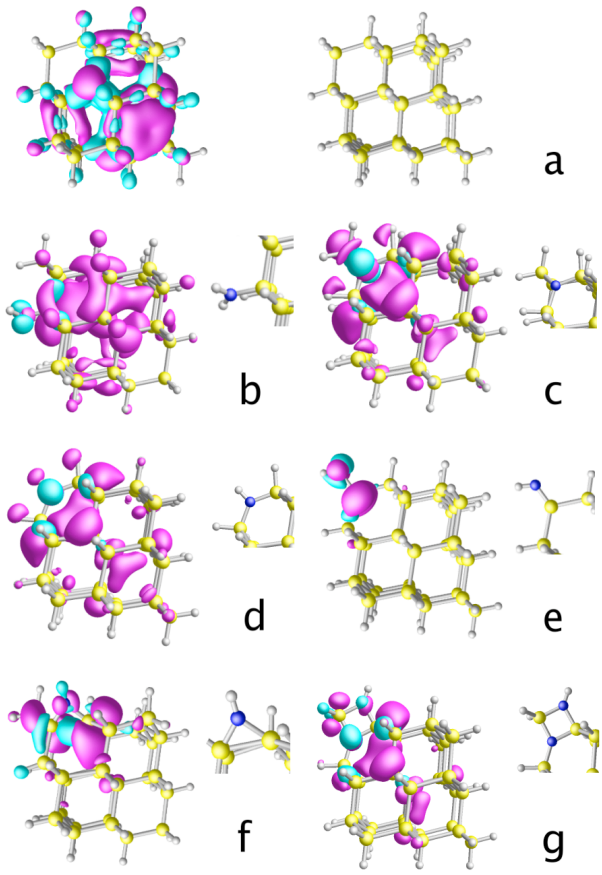

Figure 3: Prototype structures on silicon nanoclusters with different nitrogen containing surface groups. Structure (a) is $Si_{35}H_{36}$, a diamond structure silicon nanoparticle terminated with hydrogen. Structures b-g contain different nitrogen containing surface groups.

4 FIRST PRINCIPLES MODELING OF THE OPTICAL RESPONSE OF SILICON NANOWIRES

The continued scaling of silicon transistor performance, new FinFET architectures based on silicon or Ge are under research and development. When the minimum dimensions of crystal Si nanostructures are scaled below ~10nm, it is anticipated that quantum confinement effects will begin to influence their dielectric response. This poses a challenge to optical metrology techniques which in current practice assume bulk behavior for the silicon optical response when modeling the spectral signatures of diffracted or scattered optical beams. One such optical metrology is optical or spectroscopic scatterometry, which monitors the geometric profiles of periodic structures during semiconductor device fabrication by solving the inverse scattering problem.

To gauge the measurement bias in these measurements, we have used first-principles density functional theory

approaches to calculate the size- and shape-dependence of the optical response in silicon nanostructures.

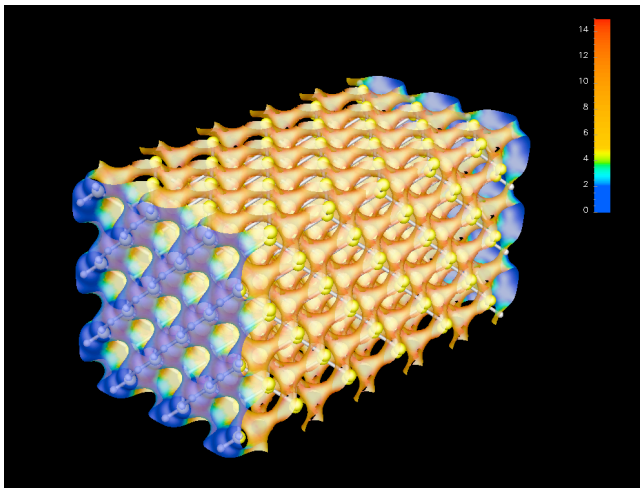

Figure 4: Static dielectric response inside a silicon slab. The blue colored surfaces are the surfaces of the slab, where the dielectric response drops to 1. Periodic boundary conditions are applied perpendicular to the surface.

Figure 4 shows a density functional theory calculation of the dielectric response of silicon slab terminated on the surface with hydrogen atoms. The colored isosurfaces show the magnitude of the dielectric response. This ranges from 1 in the vacuum to 13 in the middle of the slab. The dielectric response is concentrated in the regions of high density, such as in the middle of the covalent bonds.

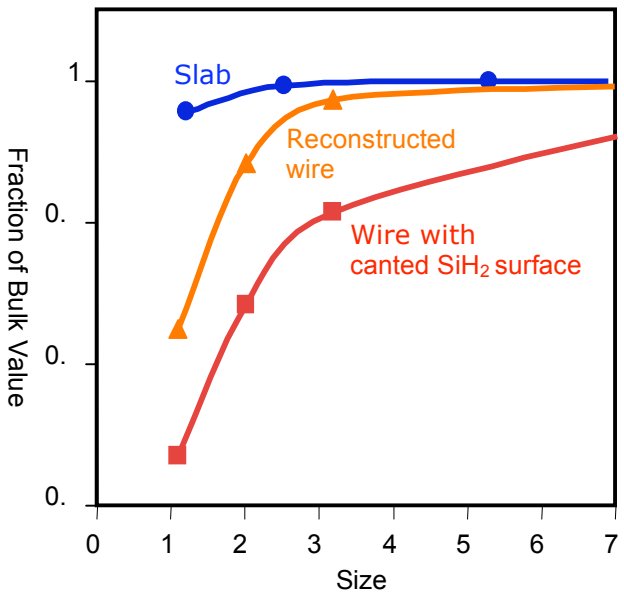

Figure 5: Size dependence of static the optical response of silicon slabs and nanowires with different surface structures.

Figure 5 shows the calculated static dielectric response in the middle of a silicon slab or nanowire as a function of slab thickness or nanowire diameter. It shows a strong size dependence of the optical response of silicon nanostructures with critical dimensions smaller than 5 nm. In this size regime the size dependence is stronger for 1D silicon nanowires than for 2D slabs. We also observe a strong dependence of the optical response with the surface structure of the silicon nanowires.

These results suggest that for nanostructures larger than 5 nm the standard optical scatterometry approach should continue to work adequately. For smaller nanostructures, accurate calculations of the dielectric response will be required to predict how light is scattered.

Additional calculations to predict the frequency dependence of this dielectric response in silicon nanostructures are currently underway.

5 ACKNOWLEDGMENTS

I would like to thank my collaborators Francois Gygi, Giulia Galli, Sebastien Hamel, John Reed, Trinh Vo, and Hugh Wilson. This work was performed under the auspices of the U.S. Dept. of Energy at the University of California/Lawrence Livermore National Laboratory under contract no. W-7405-Eng-48.

REFERENCES

[1] A. Majumdar, Science, 303, 777(2004).
[2] N. Mingo, L. Yang, D. Li, and A. Majumdar, Nano Lett. 3, 1713 (2003).
[3] T. Vo, A. Williamson, and G. Galli, Phys Rev B 74, 045116 (2006).
[4] L. Dal Negro, J.H. Yi, L.C. Kimerling, S. Hamel, A.J. Williamson, and G. Galli, Appl. Phys. Lett. 88, 183103 (2006).