Summary of 5th Year Program Review

The 5th year review for MURI program was held in San Diego Loews Coronado Bay Resort from March 24-27, in conjunction with the DARPA program review and the DOE High Efficiency Thermoelectrics Workshop. The review of our MURI program was held on March 25. Review panel members include Dr. John Pazik, Dr. Kathryn Wahl, and Dr. Valerie Browning. All Co-PIs except Professors Wang and Goorsky attended the review. Professor Wang suffered from a broken leg in Hong Kong and sent in associate, Dr. Jianlin Liu, to make a group presentation in his absence, and Professor Goorsky canceled his attendance due to a last minute flu.

The review panel thinks that the program has made important contributions in the fundamental sciences of thermoelectrics in low-dimensional structures, particularly regarding electron and phonon thermoelectric transport in nanostructures. The program started 5 years ago with the idea of low-dimensional (2D) quantum structures along the in-plane direction but has moved well beyond these early approaches to address emerging issues in low-dimensional thermoelectrics, such as phonon transport and nanowire structures. The review panel expressed pleasure in seeing that our group members have worked as team and have produced many good papers and students and have had an impact on the field. The review panel raised the following questions.

1. What are the big pictures scientifically and technologically?

   Answer: I will use the reflection I circulated to start our discussion and eventually incorporate into our final project report.

2. What work and what did not work?

   Answer: Again, see my reflection.

3. How to best utilize the remaining few months of the no-cost extension, particularly in Si/SiGe area, in nanowires, thermal management issues, and Hi-Z results.

   Answers: In the Si/SiGe area, the Chen group's goal is to finish the measurements of anisotropic thermal conductivity, anisotropic Seebeck coefficient, and in-plane electrical conductivity of the samples recently grown by Wang's group, and to push all the measurements to a to higher temperature range, up to 200 ^{o}C, to examine the unusual trend in the anomalous rapid rise in the Seebeck coefficient.

   On nanowires, Berkeley's recent idea of a 1° beveled surface provides a potential way to measure the electrical conductivity and contact resistance. This idea can have a major impact on doing science for both the temperature dependent resistivity and magnetoresistance for Bi and $Bi_{1-x}Sb_x$ nanowires. We will further explore this new development and combine it with recent developments in the

Chen and Dresselhaus groups on thermal diffusivity and Seebeck coefficient measurements to obtain our first determination of the ZT of nanowire arrays in templates.

On Hi-Z's results, Chen's group will obtain Hi-Z samples and carry out experiments to see whether they can reproduce the Hi-Z results. The Dresselhaus group will look into B_4C materials from a theoretical point of view.

On the thermal management issue, Chen's group will work with Fleurial and Lyon to produce regime maps such that the thermal management issues can be clearly mapped with film thickness. This project has a high pedagogic component. Some other group members may participate.

In the modeling area, Chen's group will aim at establishing a unified phonon transport model covering both coherent and incoherent phonon transport regimes and the Dresselhaus group will continue to develop their models on segmented nanowires. The message that Angie Stacy can provide us with actual segmented $Bi/Bi_{1-x}Sb_x$ nanowire samples will strongly influence our planned research on segmented nanowires.

Major Achievements of MURI Project

One area that we have made significant impacts is the understanding of fundamental science of thermoelectricity in nanostructures. When we started in 1997, the ideas of electron and phonon engineering for thermoelectric applications just emerged. Through this project, we have put some of these ideas on solid grounds through combined theoretical and experimental studies. For example, in the electron transport area, Dresselhaus' group confirmed the prediction of semiconductor to semimetal transition in bismuth nanowires for their applications in thermoelectrics, and developed the concept of carrier pocket engineering for utilizing the real estate of all layers in a superlattice for enhancing three-dimensional figure of merits. Experimental studies carried out by Chen in collaboration with other team members on the thermal conductivity of superlattices, combined with the modeling carried out by Chen and Wang's groups, identify the major mechanisms for reduced thermal conductivity in superlatticesas coming from the interface reflection. Most of the existing experimental data on thermal conductivity can be explained with the models developed.

Materials are the key link between theories and experiments. Synthesis of nanostructured materials for thermoelectric applications has proven to be very challenging. Our MURI group has made significant strides in the synthesis of nanostructured materials. At the beginning of this project, the one-dimensional system (nanowires) was just on the paper for theoretical calculations. Dresselhaus group championed the templates-based methods and has collaborated closely with the Berkeley and JPL groups to develop the templates-based methods into a very popular approach. Various nanowires, including Bi, Bi_2Te_3, $CoSb_3$, BiSb have been synthesized and some of their properties are measured. In the superlattice area, our effort eventually focused onto Si/SiGe superlattices. Many issues specific to thermoelectric materials, such as the requirements on buffer composition and thickness, superlattice thickness, and electrical insulation have been addressed. The laser sputtering deposition on skutterudite-based superlattices also made significant progress in demonstrating first epitaxial growth. Hi-Z's sputtering deposition has lead to samples with intriguing properties.

Characterization of the thermoelectric properties of nanostructured materials has proven to be the most difficult task, much more than we originally anticipated. We are glad that we have made significant strides in this area. We learnt to closely couple the characterization with the synthesis processes. For example, we are able to measure the anisotropic thermal conductivity of superlattices (along and perpendicular to the film plane). These data play significant role in identifying the major mechanisms behind the thermal conductivity reduction observed in low-dimensional systems. We also are able to characterize the Seebeck coefficients along both in-plane and cross-plane directions. In the nanowire area, we have developed methods to measure the Seebeck coefficient and thermal diffusivity of nanowire arrays and method to measure the electrical conductivity of a single nanowire. In conjunction with the property characterization, the structural characterization also played a very active and important role. The TEM (Gronsky) and

X-ray (Goorsky) characterization helped significantly the initial stage of Si/SiGe superlattice growth. The TEM is also instrumental for improving the nanowire synthesis processes and helped identifying the oxidation problem associated with bismuth nanowires.

The device modeling, design, and fabrication started with low profile at the beginning as materials were being developed, and picked up speed in the last three years. Concurrent developments of materials and devices have imposed various constraints on the device effort and the Kim group's approach focused on developing fabrication processes using targeting materials including Si/SiGe superlattices from Wang's group and electroplated Bi_2Te_3 films from JPL. Chemical vapor deposition is also explored by Chen's group. These efforts aim at transport alone the films. In the last two years, Goorsky's group started exploring cross-plane device configuration by addressing the need of thicker samples through wafer bonding. These efforts have led to several fabrication routes for thin-film based thermoelectric devices.

Multidisciplinary students and post-docs training is an area of the greatest satisfaction of our program. The program supported 21 Ph.D. students. Among them nine graduated and two of them are currently assistant professors (Professor Zhibo Zhang at North Carolina State University and Professor Theodorian Borca-Tasciuc at Rensenlaer Polytechnique Institute). A large number of students working on MURI program are graduating this year. The program also supported 9 post-docs. Three of them are now associate and assistant professors (Associate Professor Alexander Baladin at UC Riverside; Associate Professor Sebastian Volz at Ecole Centrale de Paris; and Assistant Professor Taofang Zeng at NC State University). Many of the graduates continued doing research in thermoelectrics and nanotechnology in general. Students and post-docs have benefited tremendously from the multidisciplinary training, from interactions with other faculty members, other students, our industrial partners and industrial advisors. They learnt how to do multidisciplinary research and had opportunities to meet review panel members and program managers during the review processes. Such rich experience will no doubt help them in their future endeavor.

The multidisciplinary research program also has also impacts outside our proposed research programs. We will list only a few examples here. Dresselhaus templates approach has been widely used in various efforts to make nanowires. Berkeley has developed a very active nanowire program through collaboration with Stacy in chemistry, with Dresselhaus at MIT, and with Fleurial at JPL. Chen has developed two research projects with JPL on thermoelectrics through the collaborations established in this program. Chen has brought Lockheed Martin and the Berkeley together to develop a new nanowire program. The modeling tools established for phonon transport modeling has greatly impacted the field of nanoscale heat transfer. Chen's group helped Motorola to develop a thermal conductivity measurements system for their thermoelectrics program.

Major Disappointments

Our major disappointment is on ZT values. Although two groups (Lincoln lab and RTI) have reported significantly higher ZT values in superlattice (or quantum dots superlattice) systems, the difficulties we encountered in the synthesis and characterization of Si/SiGe materials and nanowires has not given us high ZT values as we anticipated. But we think the program has made good progress in solving these problems. Results and ideas generated through this program have helped the field in general. Some specific results and ideas we have are worthy continuations. Hi-Z's results suggest high ZT values but we need to carry out further validation work. Particularly, our effort in the last few months will be very important.

Another specific disappointment is on the electrical contact resistance issue. This has turned out to be detrimental for the electrical conductivity determination of superlattices (cross-plane directions) as well as nanowires. Although our studies have pointed some of the sources for the large contact resistance, we have not fully solved this problem.