1. RESEARCH AND SCHOLARSHIP

1.1 Summary of Research Thrusts and Accomplishments:

The broad area of my research is the study of electronic materials with thrusts in temperature dependent electronic and thermal transport measurements, thermoelectric materials and devices, and the growth and application of nanowires. My contributions have included being a co-editor for 4 books, writing two book chapters, a patent, 48 journal publications, and 49 conference papers. I have given several invited presentations and helped organize 3 symposia and a workshop on thermoelectrics. My papers have been cited approximately 1,159 times with an average of 24.6 citations per paper (3.27 citations per paper per year), and an h-index of 17 (as given by the ISI Web of Science). In the remainder of this section please find a summary of my research contributions and future plans.

1.1.1 Thermoelectrics

My research goals have included establishing a state of the art electronic materials laboratory with transport measurement systems for temperature dependent characterization, and to develop a pulsed laser deposition system for the fabrication of thin films and for the growth of nanowires. Through this effort we have established a number of measurement capabilities for electrical and thermal transport over the 4.2K to 1000K temperature range. These capabilities include over 7 independent transport measurement systems for temperature dependent measurements including: Electrical Conductivity (4.2K - 1000K), Thermoelectric Power (4.2K - 1000K), Thermal Conductivity (4.2K - 400K), Current vs. Voltage (4.2K - 800K), Hall Effect (4.2K - 400K), High Temperature System (4.2K - 800K), ZT meter for up to 16 samples at a time (room temp), Scanning voltage probe (50μm resolution) measurements (room temp). In addition, three systems for thermoelectric module characterization are bell jar, and small vacuum chamber based systems for long term characterization. A larger diameter (6") furnace is used for diffusion bonding, and annealing studies. Diamond wheel saws (low speed, and CNC), and a sample polishing system are some of the pieces of equipment for sample preparation. A Netzsch DSC/TGA/MS system for thermal analysis and mass spec. measurements has capabilities from room temperature to >1000°C. In addition a pulsed laser deposition system based on a Lambda Physik LPX210i Excimer Laser (248nm, 25ns, 1000mJ) has been established for deposition of thin films and multilayers that can be used for coatings and interface studies. It has also been used in the growth of oxide based nanowires.

Much of my work in thermoelectrics has been collaborative in nature promoting interdisciplinary interactions between research teams. This has been very fruitful toward the production of publications, patents, and technology transfer. It has been an invaluable experience for students, researchers, and faculty who regularly interact with others having backgrounds ranging from physics ([redacted] UofM), chemistry ([redacted]), electrical engineering (myself[redacted], mechanical engineering ([redacted] MSU), and materials science ([redacted] MSU). Such multidisciplinary efforts have helped to establish Michigan State University as a one of the leaders in the area of thermoelectrics. This has helped in attracting additional funding and for hiring new faculty [redacted] with similar and complementary research interests. My specific contributions to these research efforts have focused on the temperature dependent characterization of new bulk materials, the development of low electrical resistance contacts to the thermoelectric materials, the fabrication and testing of thermoelectric modules, and modeling of the modules based on the transport properties.

Materials: Thermoelectric materials are used to fabricate modules by electrically connecting legs of n-type and p-type materials in series, typically in an array pattern such that they are also thermally in parallel. Supplying electrical energy to such modules will produce a temperature gradient across them, and conversely by supplying thermal energy to the modules, then electrical power will be produced. Such power generation devices have commonly been used in satellite power systems and have been of great interest recently for terrestrial applications. These modules are most efficient when the properties of the thermoelectric materials used show high electrical conductivity, σ, high thermopower (absolute Seebeck coefficient), α, and low thermal conductivity, κ. A measure of the effectiveness of such materials is the unitless figure of merit, ZT, such that ($ZT= \alpha^2\sigma T/\kappa$). For temperatures &900K, the combination of such properties is commonly found in narrow bandgap semiconductors. Traditional materials such as bismuth telluride, lead telluride, and silicon germanium have relatively low efficiency of power conversion, and significant research effort to increase this efficiency has recently gone into the discovery, fabrication, and development of new materials and new processing techniques. Such research has led to the discovery of several chalcogenide based thermoelectric materials which show some of the highest figure of merit values known for the temperature range of 500-850K as shown in Figure 1.

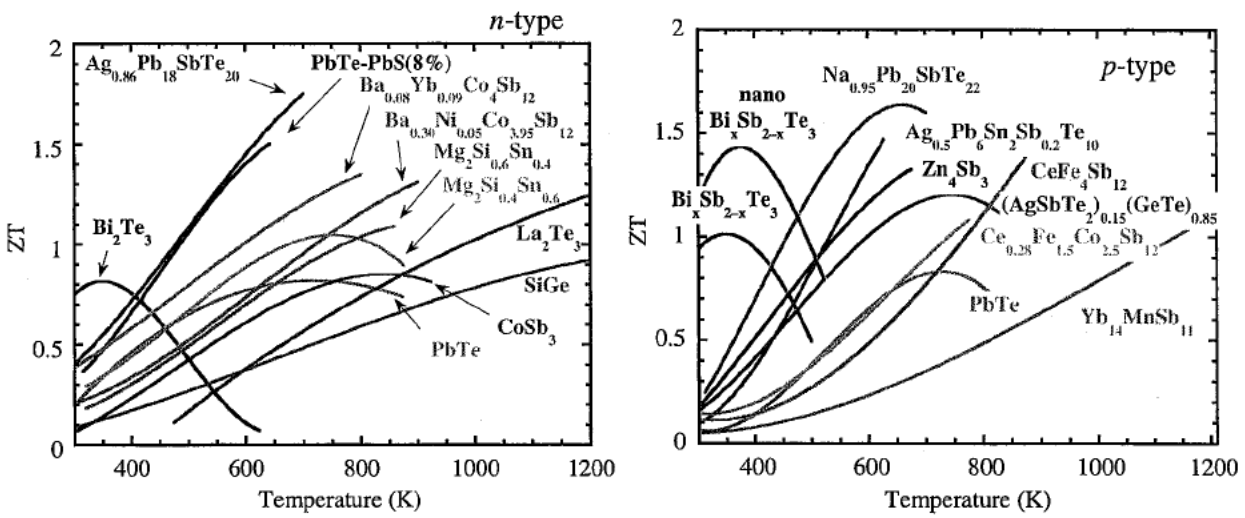


Figure 1. Best known thermoelectric materials for n-type and p-type samples. The high ZT materials fabricated by [redacted] and measured by us include the $Ag_{0.86}Pb_{18}SbTe_{20}$, PbTe-PbS(8%), $Na_{0.95}Pb_{20}SbTe_{22}$, and $Ag_{0.5}Pb_6Sn_2Sb_{0.2}Te_{10}$ compounds which are the highest performance n-type and p-type materials shown for the 500-700K temperature range.

Electrical Contacts: We are now in the process of working to scale up the production of these high ZT materials and develop them into prototype modules in order to study the fundamental issues associated with the processing, the fabrication of contacts, and with the module design and measurements. My group has been particularly focused on the contacts, module development, and module measurements. My group has achieved the fabrication of low resistance contacts to the thermoelectric materials being investigated including contact resistivities less than $20(\mu\Omega\cdot cm^2)$ to metal contacts, and less than $5(\mu\Omega\cdot cm^2)$ junctions to bismuth telluride materials for segmented module structures. Through our efforts, to systematically reduce the contact resistivities the efficiencies of prototype modules based on these new thermoelectric materials have increased from values of less than 1% to greater than 4%. Contact resistances have achieved values that should lead to efficiencies greater than 10%, however a significant contribution to parasitic resistance losses has been due to cracking in the materials. Increases in strength are being addressed through studies by [redacted] group of powder processing of these materials where we have seen a three fold increase in strength of hot pressed samples compared to cast materials.

Measurements: Accuracy in the measurements is of crucial concern and collaborative efforts between research groups are essential to validate the measured properties of materials, and to test the measurement techniques and their limitations. To that end, my group has participated in a round robin effort organized by NIST to identify a thermopower standard. A publication has been prepared by the NIST group describing this collaborative effort and measurements of undoped Bi_2Te_3 and constantan samples and is to be submitted to the Journal of research of the National Institute of Standards and Technology. My group has also worked to measure the various properties using separate and overlapping measurement systems and techniques. For example, we measure the room temperature voltage profile on a sample to measure the contact resistance and the resistance of the sample. This is compared to the measured room temperature electrical conductivity found in our temperature dependent measurement systems using the standard 4-probe measurement technique. We have also established a ZT meter which directly measures the figure of merit of the sample at room temperature and at lower temperatures. In collaboration with [redacted] Lab, we have tested this technique to higher temperatures and found it to be dependent on the emissivity of the sample (constantan gave good agreement with literature values to 700K, however SiGe samples showed significant radiation effects above 450K). Below ~ 450K, however the direct ZT measurement can be used to validate the measurements of electrical conductivity, thermopower, and thermal conductivity that we measure individually. Such overlapping measurement techniques are very effective in checking the accuracy of the measured samples. In addition, the ZT direct technique has provided a means of testing a number of samples at room temperature as the mounting configuration follows the standard 4-probe technique. Based on this measurement we have developed a 16 sample measurement system and utilized it for composition variation studies.

Thermoelectric materials, and the studies discussed above, cover a range of disciplines and processing challenges that are highly beneficial for graduate students and postdocs to be exposed to. This has helped researchers to gain insight on the steps necessary for bringing new materials to the prototype fabrication level. This work has been supported by the Office of Naval Research – Science and Technology Division through a Multidisciplinary University Research Initiative (MURI) program, and through a grant from the Department of Energy – Energy Efficiency Renewable Energy (EERE) Division.

1.1.2 Nanowires

While the largest focus of my time and effort in research has been in the area of thermoelectrics, I have also worked on the area of nanowire fabrication as an independent focus of research.

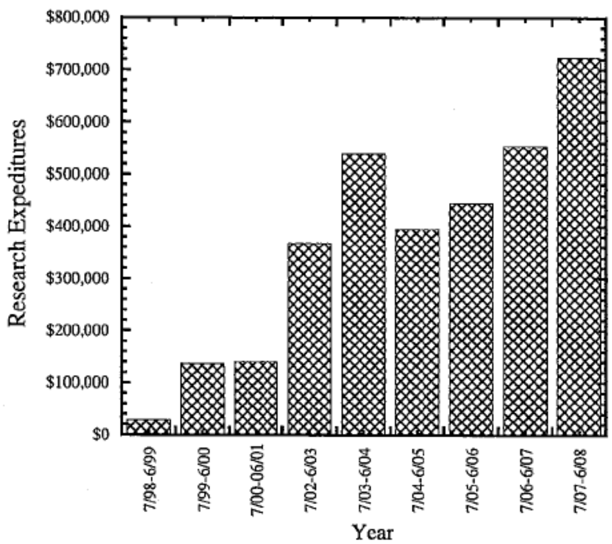
Nanowire Growth: In this effort we have investigated the fabrication of zinc oxide and germanium dioxide nanowires grown by the vapor-liquid-solid (VLS) technique. In this technique a metal catalyst (typically gold, iron, and/or nickel, however other metals also work), is used to guide the growth of nanowires by forming a eutectic with the material being grown. The eutectic forms at a relatively low temperature and thus the alloy formed remains liquid during the growth process. This wet spot on the substrate has a high sticking coefficient for incident source material, and supersaturation of the alloy occurs. At supersaturation, a solid drops out of the liquid alloy to form the next layer along the length of the nanowire, thus moving the alloy out of the supersaturation region of the phase diagram. This process repeats as the nanowire continues to grow in length with a diameter defined by the size of the liquid droplet at its tip. Through an NSF Career Award, we developed the methods and systems for nanowire fabrication [[1]]. Nanowires of zinc oxide and germanium dioxide have been particularly promising for consistency and quantity of nanowires formed.

Surface Enhanced Raman Spectroscopy (SERS): Collaborations were formed with [redacted] (ECE, MSU) after discussions of surface plasmon excitations on randomly rough metal surfaces. Through an NSF NER grant, we investigated metal (primarily gold) coated nanowires for surface enhanced Raman spectroscopy (SERS). In Raman spectroscopy, laser light interacts with the vibration modes of the molecules to either gain, or lose some energy. The resulting shift in wavelength of the reflected or transmitted light is the measured Raman spectrum and is a fingerprint for the molecule detected. Such interactions occur for approximately one in one billion photons incident on the sample. SERS enhances this interaction by different mechanisms including an electromagnetic enhancement. With surface plasmon

1 [redacted] "Growth of Si wires on a Si(111) substrate under ultra high vacuum condition," *Journal of Vacuum Science and Technology B*, vol. 22, no. 1, 2004.

waves, the electric field which is close to the surface of the metal interacts with the molecules absorbed on the metal surface and enhances the Raman effect. We found for adsorbed SERS reference molecules (such as nile blue), enhancement factors of approximately 10^6 were possible at various locations, or "hot spots", on the substrate. Such hot spots are commonly found in the literature on SERS. With reference analytes that form self assembled monolayers on the gold coating (such as 4-methylbenzenethiol (4-MBT)), we found the enhancement factors were uniform over the substrate at approximately $10^6 \pm 20\%$ [[2]]. Through TEM studies it was further found that the gold coatings on the nanowires did not form continuous films, but followed island growth with gold particles in the 2-10nm diameter range. The ease of fabrication (no regular arrays needed) and good uniformity over the sample could be a significant advantage for the application of these nanowires. Electromagnetic modeling of the surface plasmons for this system has been imitated to investigate the possibility of further increasing the enhancement factor through dimensional changes of the nanowires, and/or surface coverage of the wires with gold.

Through these research efforts, the research expenditures, and number of citations of our work have increased over the years as shown in Figure 2.



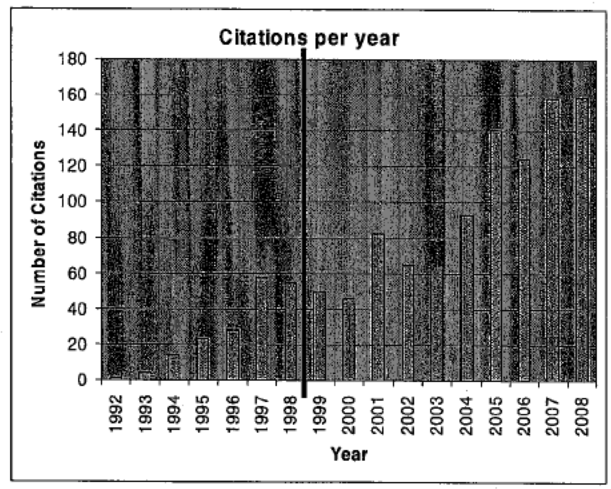


Figure 2. Research expenditures and number of citations per year. The dark line in the figure on the right shows the year I started at Michigan State University (1998).

1.2 Future Efforts:

1.2.1 Research

In my research goals, I would like to continue the development of thermoelectrics through material characterization for an increased understanding of these materials, and the development of power generation modules to find solutions to remaining challenges hindering their application. By its nature this is a multidisciplinary problem, however I am also working toward generating more journal articles based on the specific efforts of measurements, contacts, and module development from my group. I believe the thermoelectrics group at Michigan State University is ready for center level activity, and I would like to be instrumental in obtaining such support. More specifically, concentrated efforts in the following areas of research related to thermoelectrics are of interest:

1. **Electrodes and Contacts**: There is a general need in thermoelectrics and in wide bandgap semiconductor research for improved understanding of forming low resistance, stable electrical

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[2] [redacted] "Surface-Enhanced Raman Scattering from Gold Coated Semiconducting Nanowires," *Journal of Raman Spectroscopy*, vol. 39, no. 7, pp. 893-900, 2008.

interconnects. We have initiated research in this area, however there is much yet to be done. Much of the electrode materials and contact interface materials are based on exploratory research based on thermal expansion coefficients, high temperature stability, oxidation resilience, electrical and thermal resistances, etc. A stronger effort on the theoretical guidance of thermodynamics, chemical interactions, diffusion constants, expected doping effects, and phase diagrams backed with experimental validation of the calculations could significantly aid in directing the selection of optimal electrode materials and diffusion barriers for new materials. Additional efforts in finite element modeling of the system would further aid in the physical design of the electrodes to accommodate thermal stresses, and identify engineered solutions to such limitations – including spring loaded pressure contacts with liquid metal interfaces, and finger electrodes to accommodate expansion and compression. Such studies should be applicable to other materials such as wide bandgap semiconductors that can be used at higher operating temperatures.

2. **Energy Conversion Studies**: Thermoelectrics provides an avenue to direct thermal to electrical energy conversion. It can provide improved efficiencies to existing systems either by extracting more energy from the waste heat for direct use, or by using the energy extracted to further improve the efficiency of the process used by the system it is attached to. For example, [redacted] has developed a wood burning stove that utilizes a thermoelectric generator to enhance the efficiency of the stove by blowing air into the combustion chamber [[3]]. I am interested in investigating similar, system wide considerations of efficiency enhancements which could be applicable to applications such as coal plants, internal combustion engines, solar cells, and residential cogeneration systems.
3. **Sensors and Detectors**: The nanowire research I have pursued was initiated to develop sensitive detectors for biological and chemical sensing purposes. Initial efforts focused on site specific growth of nanowires in the attempt to fabricate the sensors by growing nanowires between pre-defined electrodes, followed by functionalization of the nanowire to establish field effect devices for detection of an adsorbed molecule of interest. There has been some success in the growth of nanowires at locations where a metal catalyst has been deposited, however the next steps will require better control of how the nanowires grow, and the appropriate termination of the nanowires into a secondary electrode. To that end, I have been working with a colleague [redacted] in attempts to study the effects of external forces applied during the growth of nanowires. These might include electric, magnetic, and temperature gradient forces (induced optically for example). Theoretical modeling along with experimental testing of the theories is of interest for future research. Both electrical and optical detection schemes are of interest and I would like to expound on our efforts of utilizing nanowires for SERS studies to investigate possibilities of higher enhancement factors.

1.2.2 Teaching:

During my time at Michigan State University, I have taught 9 different courses, and I am presently teaching a new graduate level cleanroom course which utilizes the ECE Cleanroom (I redesigned, and oversaw the renovation of this cleanroom). There are many outstanding instructors within the ECE Department at MSU, and I have gained much through discussions and interactions with them. I have striven to engage the students within the courses I have taught through active learning techniques, and hands on activities. I have also spearheaded efforts to use tablet computers for delivering class notes and placing those same notes on the course website for the students to access. In some classes, I have asked honors option students to fabricate various circuits or experiments and give a presentation to the class so the learning experience extends beyond the honors option student alone. In lower level courses I have utilized my office hours to have students in the course gain hands on experience with soldering. I have also worked hard to give all students an equal opportunity in the course by providing old exams to everyone for studying purposes. I have utilized technology to aid in studying of crystal structures as seen on my website [redacted] These techniques have been well received by the students, and although I ask much of them in the courses, they are very appreciative of such efforts. In the future, I would like to incorporate a few more in-class activities for some additional variety (particularly

[redacted]

later in the semester). I would like to help develop several new courses associated with energy conversion, and to expound on the cleanroom course with additional experiments and lecture material.

1.2.3 Public Service:

I have co-organized three Materials Research Society symposia related to thermoelectrics in 2003, 2005, and 2007 – taking the lead role in the last one. The interest in these symposia has consistently grown as evidenced by the continually increasing number of abstracts submitted. This has also necessitated higher selectivity of submitted abstracts reaching rejection levels above 20% in 2007. These have all resulted in publication of the symposium proceedings in the standard MRS Symposium Proceeding blue books. In 2002, I co-organized a workshop on thermoelectrics which also resulted in a book that was published. I have also been active in article reviews for a number of journals, and proposal reviews for NSF and CRDF.

As advisor to the IEEE Student Branch, I have seen this organization grow over the years. We are actively bringing companies on campus to present to the IEEE members, with a specific emphasis on hands on demonstrations, and technical presentations about problem solving. We have worked to bring Student Professional Awareness Conferences (SPAC) to campus with outside speakers covering topics of professionalism, job expectations, and entrepreneurial advice. We have worked in small project groups to study how scanning tunneling microscopes are fabricated, and in other groups to give the general members soldering experiences. We have also been active in outreach activities associated with Habitat for Humanity, Extreme Makeover Home Edition (home in Holt, MI), and other fundraising activities on campus.