2016 Project Abstract
For the Period Ending June 30, 2019

PROJECT TITLE: Waste Heat Recovery with Efficient Thermoelectric Energy Generators
PROJECT MANAGER: Uwe Kortshagen
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FUNDING SOURCE: Environment and Natural Resources Trust Fund
LEGAL CITATION: M.L. 2016, Chp. 186, Sec. 2, Subd. 07b

APPROPRIATION AMOUNT: $400,000
AMOUNT SPENT: $400,000
AMOUNT REMAINING: $0

Sound bite of Project Outcomes and Results
The work performed under this project has made important contributions to the scientific community, documented in several scientific papers, and may lead to the production of new thermoelectric materials that convert waste heat into electricity. This has the potential to improve the efficiency of thermal cycles and reduce the energy lost in waste heat, which will ultimately benefit Minnesota citizens and all of humanity.

Overall Project Outcome and Results

Any thermal cycle, from combustion engines, to power plants, to refrigeration cycles produces waste heat that is not utilized but released into the environment. This project dealt with the fabrication of new thermoelectric materials, which are capable of converting part of that waste heat into electricity. The specific focus was on alloys of silicon (Si) and germanium (Ge), which are suitable for high temperature applications up to approximately 1,000 °C (approx. 1,830 °F). The focus of this project was on forming nanostructured materials that improve the thermoelectric performance by reducing the thermal conductivity of the material through scattering of heat conducting lattice vibrations at the abundant grain boundaries, without negatively affecting the electrical conductivity.

Initial work focused on forming bulk thermoelectric materials by sintering SiGe nanocrystals, particles with the size of only a few nanometers, into dense solids. However, this approach was found to be unsuccessful due to the brittleness of the material. Laser sintering of nanocrystals into thin film materials proved to be a much more successful approach, as it produced non-brittle thermoelectric thin films, with performance comparable to the best SiGe materials previously reported in the literature. Furthermore, laser sintering was found to be a fast, high-throughput method which has the potential to be applicable in industrial processes.

The porosity of laser-sintered films was identified as a potential weakness. To overcome this issue, the team developed a new approach to from nonporous nanocrystalline thin films by first plasma depositing amorphous (non-crystalline) SiGe materials, and then using thermal annealing to transform these into nanocrystalline materials. This approach was found to yield virtually fully dense thermoelectric materials with good performance characteristics and the promise of low-cost production.

The work performed under this project has made important contributions to the scientific community, documented in several scientific papers, and may lead to the production of new thermoelectric materials that convert waste heat into electricity. This has the potential to improve the efficiency of thermal cycles and reduce the energy lost in waste heat, which will ultimately benefit Minnesota citizens and all of humanity.

Project Results Use and Dissemination

By the time of the project final report, results of this research have been disseminated in seven scientific journal publications and through five presentations at international conferences.

Environment and Natural Resources Trust Fund (ENRTF) M.L. 2016 Work Plan

Date of Report: August 16, 2019

Date of Next Status Update Report: June 30, 2019

Date of Work Plan Approval: June 7, 2016

Project Completion Date: June 30, 2019

PROJECT TITLE: Waste Heat Recovery with Efficient Thermoelectric Energy Generators

Project Manager: Uwe Kortshagen

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Total ENRTF Project Budget:		
	ENRTF Appropriation:	**$400,000**
	Amount Spent:	**$400,000**
	Balance:	**$0**

Legal Citation: M.L. 2016, Chp. 186, Sec. 2, Subd. 07b

Appropriation Language:
$400,000 the second year is from the trust fund to the Board of Regents of the University of Minnesota to develop thermoelectric energy generators using advanced, high-performance materials able to more efficiently capture waste heat and transform the heat into electricity. This appropriation is subject to Minnesota Statutes, section 116P.10. This appropriation is available until June 30, 2019, by which time the project must be completed and final products delivered.

I. PROJECT TITLE: Waste Heat Recovery with Efficient Thermoelectric Energy Generators

II. PROJECT STATEMENT:

The U.S. used ~97 quadrillion BTU of energy in 2011, of which 55.6 quadrillion BTU were emitted as "waste heat" (rejected energy).[1] Tapping into this reservoir of waste heat would allow lowering the consumption of fossil fuels and reducing greenhouse gas emissions and air pollution. Thermoelectrics (TE) seeks to capture some of the waste heat and transform it into useful electrical energy.

Thermoelectric materials exhibit the unique property that a voltage is generated over even the smallest temperature difference. This voltage arises as electrons move from the hot to cold side of the material, turning waste heat into electrical energy. This property can be employed in thermoelectric generators as is shown in **Figure 1 (section IX)**. Researchers found that fabricating thermoelectric materials from nanometer-sized grains of the material (ranging from 40-400 billionths of an inch) can significantly enhance their quality. In such "nanograined" materials, electrical energy can travel largely unimpeded by the grain structure, but thermal energy (heat) is hindered by the many boundaries between the nanometer-sized grains, reducing wasted energy.

The **objective** of this proposal is to **develop more efficient "nanograined" thermoelectric materials**. Professor **Kortshagen**'s group at the University of Minnesota developed a novel synthesis technique for nanograined materials in 2005, which has since been adopted by many academic research groups throughout the world, covered by three US patents, and was licensed to companies including DuPont-Innovalight and Dow Corning.

Silicon and germanium, known as excellent thermoelectric materials for high-temperature applications, will be made into nanograins using Professor **Kortshagen**'s plasma synthesis approach. They will be densified into macroscopic nanomaterials through a heating process called thermal sintering. The resulting nanograined materials will be characterized for their thermal properties (Prof. **Wang**) and electrical properties (Prof. **Kortshagen**) to probe their efficiency. The University of Minnesota's innovative approach will enable the team to produce unique materials that may significantly advance the efficiency of silicon-germanium based thermoelectric devices.

III. OVERALL PROJECT STATUS UPDATES:

Project Status as of January 1, 2017:

During this project period, significant progress has been made toward the project goals. An existing plasma reactor was modified and new process recipes were developed to produce the amounts of materials required for the studies planned under this research project. Diagnostic methods were developed to characterize the thermoelectric materials to be studied. This includes measurements of the materials' thermal conductivity, electrical conductivity, and their "thermopower," which measures the materials' ability to produce electrical power from thermal energy. The project team also made progress on evaluating viable routes to producing bulk materials of nanograined TE materials through spark plasma processing, by leveraging on collaborators at the University of Houston.

Project Status as of July 1, 2017:

During this project period, significant progress has been made toward the project goals. Using the plasma reactor modified during the previous project period, first thermoelectric materials samples were successfully produced. Two different approaches for the sintering of the materials were evaluated. Laser sintering of thin films of silicon:germanium (Si-Ge) samples led to promising results, while the sintering of bulk materials using spark plasma sintering proved to be challenging. The first materials samples produced by laser sintering exhibited promising thermoelectric properties. Because the deposition of thin Si-Ge thin films from the plasma reactor is

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[1] Report by Lawrence Livermore National Laboratory: https://www.llnl.gov/news/americans-use-more-efficient-and-renewable-energy-technologies

very fast and laser sintering is a method that is compatible with fast fabrication approaches, this technique was deemed promising for further studies.

Along with materials synthesis and sintering of our proposed Si-Ge TE samples, the team has made significant progress on developing the pump-probe system for thermal characterization. Validation measurements have been performed on some reference materials that are also TE candidates, including doped perovskite oxides and nano-porous indium gallium nitride, which set up a baseline of materials' TE performance for further comparison. The preliminary data were quite promising and have generated two publications with LCCMR support acknowledged. Our initial efforts on the thermal characterization of reference materials have well justified the promise of utilizing our unique pump-probe technique for future studies of Si-Ge TE materials.

Project Status as of January 1, 2018:

The team conducted systematic studies to optimize both the thermal and electrical properties of TE thin films consisting of boron (B)-doped Si-Ge nanoparticles. To achieve this, the team first designed a compaction method to process the samples that allows for electrical conductivity, thermal conductivity, and Seebeck coefficient measurements. This compaction method has proved to produce sufficiently smooth Si-Ge thin films for both thermal characterization with the ultrafast pump-probe technique, as well as the electrical-conductivity and Seebeck-coefficient measurements with simple mask deposited electrodes. Initial measurements of the thermal conductivity of B-doped $Si_{80}Ge_{20}$ films were very promising. The thermal conductivity of these TE materials ranged from 0.5 to 0.62 W/m-K depending on the exact density of the film. However, electrical conductivities of the films were found to be very low. To address this issue, the team attempted intense-pulsed-light (IPL) treatment on the B-doped Si-Ge films to improve the electrical properties of the Si-Ge samples for better TE performance. It was founded that while the IPL treatment modified material structures, it did not make any apparent improvement in the electrical conductivity. Further studies will be conducted during the next period to better understand the IPL treatment effect and to scale up the PA functionalized nanoparticles. Related electrical, thermal, and Seebeck coefficient characterizations will be also carried out to provide feedback to optimize material synthesis.

Project Status as of July 1, 2018:

The team made good progress towards the project goals during this report period. Laser-sintering was found to be a good method of processing phosphorous-doped Si-Ge films, with thermoelectric properties at room temperature that are quite competitive with other approaches that require much more expensive equipment and are much faster. IPL-sintering was found to produce films with low thermal conductivity, which is desirable, but was unable to overcome problems with film porosity. The team addressed this issue with a new approach to deposit nanocrystals simultaneously with an amorphous film. The so deposited amorphous/nanocrystalline (a/nc) films were thermally annealed, leading to a crystalline material with highly desirable nanometer-sized grain structure. For 5% boron-doped $Si_{80}Ge_{20}$ films, very promising electrical conductivities were obtained. The evaluation of the thermal properties of these films and of their Seebeck coefficient are in progress.

Amendment Request (12/18/18)

Changes to the budget are requested. These changes reflect actual spending that has been different from originally budget spending, based on what was learned from the research performed under this grant.

Activity 1:

1. **Personnel:** In order to get a quick start on the project, more funds were expended on graduate research assistants than originally budget
2. **Equipment/Tools/Supplies:** For this activity, fewer costs for the modification of the plasma system than originally expect were incurred.
3. **Capital Expenditures:** Through this research initially working with external partners, we discovered that hot-pressing was not an effective means of producing thermoelectric materials. Hence, the originally budgeted hot-pressing system appearing under was not purchased.

4. **Other:** Higher expenses were incurred for the use of the Materials Characterization Facility and the Minnesota Nano Center.

Activity 2:

1. **Personnel:** Fewer expenses were incurred for graduate research assistants, since some of the students working on the project were partly working as teaching assistants.
2. **Other:** Higher expenses were incurred for the use of the Materials Characterization Facility and the Minnesota Nano Center.

Amendment Approved by LCCMR 12/18/2018

Project Status as of January 1, 2019:

The team has continued to make good progress towards the project goals. In previous activities, laser-sintering was identified as a suitable method to produced thermoelectric materials from phosphorous-doped $Si_{80}Ge_{20}$ nanocrystal films. These films have shown thermoelectric properties similar to other Si-Ge materials processed with state-of-art methods, but the method investigated here has potential advantages in terms of cost and processing time. Evaluation of the full thermoelectric properties of these films with thermoelectric devices is now in progress. The team also continues the evaluation of the thermal annealing of amorphous/nanocrystalline (a/nc) films, which compared to films produced from nanocrystals offer more control over the materials properties through the tuning of the microstructure.

Overall Project Outcomes and Results:

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The work performed under this project has made important contributions to the scientific community, documented in several scientific papers, and may lead to the production of new thermoelectric materials that convert waste heat into electricity. This has the potential to improve the efficiency of thermal cycles and reduce the energy lost in waste heat, which will ultimately benefit Minnesota citizens and all of humanity.

Amendment Request (8/16/19)

Changes to the budget are requested. These changes reflect actual spending that has been different from originally budget spending, based on what was learned from the research performed under this grant.

Activity 3:

1. **Personnel:** Fewer expenses were incurred for graduate research assistants, since some of the students working on the project were partly working as teaching assistants.
2. **Other:** Higher expenses were incurred for the use of the Materials Characterization Facility and the Minnesota Nano Center.

Please see attached amended budget worksheet

Amendment Approved by LCCMR 9/26/2018.

IV. PROJECT ACTIVITIES AND OUTCOMES:

ACTIVITY 1:
Description: Nanograined Materials Synthesis

The proposed research will build on the plasma nanocrystal synthesis approach by **Kortshagen**'s group. For the synthesis of the silicon (Si) and germanium (Ge) nanograined materials, we will construct a nanocrystal deposition reactor, as shown in **Figure 2 (section IX)**. This reactor will be able to produce deposits of Si nanocrystals or Si-Ge compound materials with dopants, small amounts of impurities that can be used to improve electrical conductivity. Two plasma reactors in parallel will be installed to create mixtures of varied material compositions. Nanocrystal films whose properties can be tailored by tuning grain size, material composition, and dopant concentration will be fabricated.

After the synthesis and collection of nanocrystal materials, our research will concentrate on the process of densification of powder-like nanocrystals to form the engineered microstructures. One approach that has proved highly successful for other materials is rapid thermal sintering, which quickly heats the nanocrystal powder to create nanograin contacts without melting the material and losing its important grain structure. By increasing the heating temperature, nanograin size may be increased and tuned. This process will preserve fine details in the material's microstructure that decrease thermal conductivity while controlling grain size and improving material density, which increases electrical conductivity.

Summary Budget Information for Activity 1:

ENRTF Budget:	**$ 157,701**
Amount Spent:	**$ 157,701**
Balance:	**$ 0**

Outcome	Completion Date
1. *Construct plasma synthesis and deposition reactor*	Dec. 31, 2016
2. *Produce thermoelectric materials through deposition and sintering*	June 30, 2017

Activity Status as of January 1, 2017:

Under the current project period, significant progress has been made toward the project goals. The project team modified a plasma reactor (largely under closely associated National Science Foundation funding) to produce bulk amounts of thermoelectric materials. A reactor configuration and reactor recipes were developed to produce silicon-germanium nanocrystal compounds that are doped with boron or phosphorous. Through modification of the system and optimization of the recipes, we were able to develop routes to produce several grams of the materials to be studied. This progress enabled us to perform meaningful materials characterizations of the desired materials.

Based on our new ability to produce large amounts of nanograined materials, we made initial progress towards goal 2 under this activity. Gram scale amounts of Si-Ge compounds were produced and sent to collaborators at the University of Houston for the sintering of the materials into bulk solids using spark plasma sintering. The purpose of this collaboration is to establish the best processing regime to produce the bulk nanograined materials to be evaluated under this project. Initial studies focused on Si-Ge compounds with an 80:20 atomic composition, doped with 5% of phosphorous. We expect these materials to display good electrical conductivity, while maximizing the thermopower. The size of the nanocrystals was chosen to be 5 nm in order to reduce the thermal conductivity significantly below the bulk limit.

Based on results of our collaboration with the University of Houston, we plan to evaluate the acquisition of a spark-plasma sintering device rather than the initially planned hot pressing device. While hot pressing is an established technique to produce dense materials through the sintering of powders, spark-plasma sintering is a newer technique, which has shown an excellent ability to produce dense materials while preserving the nanostructure. Our studies over the next few months will help to establish which sintering technique is best suited for the materials studied under this project.

Parallel to the synthesis and processing studies, the project investigators have advanced their ability to characterize the thermal and electrical properties of the TE materials studied under this grant. Professor **Wang** has built up capabilities to assess the thermal properties of sintered Si-Ge TE materials using a custom-built ultrafast pump-probe system in Prof. **Wang**'s lab. Professor **Kortshagen**'s student received training to measure the thermopower of the materials studied in the laboratory of Professor James Kakalios at the University of Minnesota. Measurements of the electrical conductivity are routinely performed in Professor **Kortshagen**'s laboratory or that of Professor Eray Aydil, a close collaborator. Through these efforts, the project investigators have built up the capabilities to comprehensively assess the thermoelectric properties of the materials to be studied under this project.

Another important activity over the past few months has been the hiring and training of new students under this project. Ms. Kelsey Mork, who has been working on Si-Ge TE materials for her master thesis, is expected to graduate in summer of 2017, and is right now training a new student on the operation of the plasma synthesis system. This will ensure continuity of the research performed under this project.

Activity Status as of July 1, 2017:

During the previous project period, we had produced gram scale quantity samples of thermoelectric Si-Ge powders and worked with collaborators at the University of Houston on sintering these materials into bulk solids using spark plasma sintering. Unfortunately, these studies were to date not encouraging, because the spark plasma produced materials turned out to be very brittle. We hypothesize that the hydrogen that is bound to the nanoparticle surfaces during plasma synthesis leads to hydrogen embrittlement during the sintering process. The embrittlement problem has prevented us from determining the thermoelectric properties of these materials.

In parallel to the evaluation of spark plasma sintering, we also pursued laser sintering of the thermoelectric phosphorous-doped Si-Ge nanoparticles. Nanoparticle thin films were sintered using a millisecond pulse width, quasi continuous wave, near infrared laser at a wavelength 1070 nm. We found that the laser power and the pulse repetition frequency had a significant impact on the quality of the sintered materials.

Good film properties were found for intermediate powers and pulse frequencies. Under these conditions, the germanium rich regions produced a relatively uniform network of conductive path ways. The best parameters achieved resulted in a dimensionless figure of merit, ZT, of 0.05 at room temperature, which was quite competitive with results obtained by other researchers using different sintering methods. This is a very encouraging result, given that our studies are quite preliminary.

To better interpret these preliminary results, further studies are required. In particular, it is necessary to analyze the grain size of the sintered material and learn about the film porosity after sintering. We hope that these studies will help us to further optimize the laser sintered films. Furthermore, initial studies focused on phosphorous-doped Si-Ge samples. Work on laser sintering of boron-doped Si-Ge is currently in progress.

Another important activity is the dissemination of initial thermal studies on reference samples (oxides and InGaN) via two peer-reviewed journal publications. We acknowledged LCCMR grant for partially supporting the research work reported in those two papers (see details in **Section V DISSEMINATION**).

Activity Status as of January 1, 2018: Starting from January 1, 2018, we will be focused on **Activity 2** to optimize the TE properties of doped Si-Ge nanoparticles, using the materials synthesis and property characterization techniques developed in **Activity 1**.

Activity Status as of July 1, 2018: As of July 1, 2018, the focus of the project is mainly on **Activity 2**.

Activity Status as of January 1, 2019: As of January 1, 2019, the focus of the project is mainly on **Activity 3**.

Final Report Summary:

The project team modified two plasma reactors in Professor **Kortshagen**'s lab (largely under closely associated National Science Foundation funding). One reactor is able to produce deposits of Si nanocrystals or Si-Ge compound materials with dopants (**Figure 2 (section IX)**) while the other reactor can produce thin films of doped amorphous SiGe with SiGe nanocrystalline inclusions (a/nc films) (**Figure 3 (section IX))**.

SiGe nanocrystals with an 80:20 atomic composition, doped with 5% of phosphorous have been made via the first reactor. The size of the nanocrystals was chosen to be 5-8 nm in order to reduce the thermal conductivity significantly below the bulk limit. Three techniques were acquired for sintering the powder-like materials and producing dense bulk solids: spark-plasma sintering, hot pressing, and laser sintering. The spark plasma and hot pressing produced materials proved to be less attractive because of their embrittlement. Therefore, gram scale amounts of SiGe compounds were produced and sent to our collaborator (Professor **Gupta)** at the University of Virginia for the sintering of the materials into bulk solids using laser sintering. Nanoparticle thin films were sintered using a millisecond pulse width, quasi continuous wave, near infrared laser at a wavelength 1070 nm. Dense films produced with this method proved to have the microstructure suitable for thermoelectrics.

In the second plasma reactor, thin films of p-type boron (B)-doped amorphous SiGe with nanocrystalline inclusions of SiGe (a/nc films) were deposited on quartz substrates. The substrate was heated to 250°C during the film growth, which improved the quality of the film by providing the atoms with sufficient mobility to find a more stable and lower defect configuration. Post deposition, thin films were placed in a furnace to anneal the samples and form polycrystalline films with nanograin structure necessary for high ZT thermoelectrics. Raman spectroscopy showed three peaks for Ge-Ge, Si-Ge, and Si-Si bonds in the polycrystalline film with higher intensities as compared to the initial sample. This confirms higher crystallinity of the polycrystalline films compared to the initial a/nc films.

Parallel to the synthesis and processing studies, the project investigators have advanced their ability to characterize the thermal properties of the TE materials studied under this grant. Professor **Wang** has built up capabilities to assess the thermal properties of sintered SiGe TE materials using a custom-built ultrafast pump-probe system in Prof. **Wang**'s lab (**Figure 4 (section IX))**. Validation measurements have been performed on some reference materials that are also TE candidates, including doped perovskite oxides and nano-porous indium gallium nitride, which set up a baseline of materials' TE performance for further comparison. The preliminary data were quite promising and have generated two publications with LCCMR support acknowledged.

ACTIVITY 2:
Description: Materials Optimization

Activity 2 will focus on the optimization of the Si-Ge based TE materials produced. Initial work will focus on the structural and thermal properties of the TE materials. Materials will be probed for porosity, which is detrimental to the materials' electrical conductivity and shall be minimized. Vibrations in the nanocrystal's structure that transport thermal energy, called phonons, will be impeded to reduce thermal conductivity. This process of phonon engineering will optimize grain size and composition to reduce energy lost to waste heat.

The structural properties of the Si-Ge TE materials will be studied in Prof. **Kortshagen**'s lab, using the facilities available at the University of Minnesota Materials Characterization Facility. The thermal properties of sintered Si-Ge TE materials will be characterized with an existing custom-built ultrafast pump-probe system in Prof. **Wang**'s lab. Results will provide feedback to adjust features such as the particle size distribution, doping level, and hot-pressing temperature to reduce possible defects that may affect conductivity. Characterization will also provide guidance on the device integration as described in **Activity 3**.

Summary Budget Information for Activity 2:

ENRTF Budget:	**$ 119,898**
Amount Spent:	**$ 119,898**
Balance:	**$ 0**

Outcome	**Completion Date**
1. *Optimize boron-doped silicon and silicon:germanium TE materials*	Dec. 31, 2017
2. *Optimize phosphorous-doped silicon and silicon:germanium TE materials*	June 30, 2018

Activity Status as of January 1, 2017: We focused on **Activity 1** during this period. **Activity 2** will start after the completion of **Activity 1**.

Activity Status as of July 1, 2017: We focused on **Activity 1** during this period. **Activity 2** will start after the completion of **Activity 1**.

Activity Status as of January 1, 2018:

To optimize boron (B)-doped silicon and Si-Ge as thermoelectric materials, it was first necessary to design a method of sample processing that allows for the electrical conductivity, thermal conductivity, and Seebeck coefficient measurements of the samples. For thermal-conductivity measurements of such thin films (~ a few hundred microns), the film surface roughness has been proved to be the most challenging parameter that affects the measurement accuracy. To remedy this high surface-roughness issue, **Kortshagen**'s group incorporated a compaction method to increase the density and smooth the film surface. This method was found to sufficiently smooth the film surface for the thermal-conductivity measurements to be conducted by **Wang** using the ultrafast pump-probe technique. Initial measurements of the thermal conductivity of B-doped $Si_{80}Ge_{20}$ films were very promising, which demonstrated a low thermal conductivity of κ = 0.5-0.62 W/m-K depending on the exact density of the film.

In parallel with thermal characterization, the team has also conducted measurements of electrical conductivity and Seebeck coefficient on these B-doped $Si_{80}Ge_{20}$ films using simple mask deposited electrodes. However, initial trials showed that the electrical conductivities of the films were very low. To optimize the electrical conductivity for higher TE performance, **Kortshagen**'s group attempted intense-pulsed-light (IPL) treatment on the B-doped Si-Ge films. With the IPL treatment which sinters nanoparticles to a film, noticeable structural changes were observed in these films; however, no apparent improvements on the electrical conductivity were achieved for these films.

Finally, investigations into the dependence of the Seebeck coefficient on doping levels and alloy fractions were performed. Preliminary results suggest that there is some minor dependence of the Seebeck coefficient on small changes in the alloy fraction of the B-doped Si-Ge alloy and strong dependence, as previously suggested in the literature, on the incorporated doping level.

In the next period, the team will perform further investigations on the IPL treatment to improve the electrical conductivity and explore methods to scale up the particle. Related materials characterization of the electrical, thermal, and Seebeck coefficient on Si-Ge samples will provide feedback to further tune the nanoparticle synthesis and doping to achieve optimal TE performance.

Activity Status as of July 1, 2018:

During this period, we have continued our studies of laser sintered phosphorous (P)-doped silicon-germanium films, as these had been found to show significant promise in the previous report period. One of the most important aspects of Si-Ge thermoelectrics is their efficiency at high temperatures. After optimization of P-doped silicon-germanium films at room temperature, their thermoelectric properties (including electrical conductivity, Seebeck coefficient, and thermal conductivity) have been measured at higher temperatures. The results for figure of merit are very promising, and a paper is being prepared based on this data in collaboration with the research group of Professor **Gupta** at the University of Virginia.

In continuation of our work on materials optimization of IPL-sintered Si-Ge nanocrystal films, our team has started studying phosphorus (P)-doped $Si_{80}Ge_{20}$ films. Electrical conductivity and Seebeck measurements before IPL treatment, done by Professor **Kortshagen**'s group, show that these films could compete with B-doped Si-Ge films studied in the previous report period. Different dopant levels have been studied to tune the carrier concentration, which is a significantly important factor in thermoelectrics. P-doped Si-Ge samples with different dopant levels will be treated with IPL and first characterized at room temperature.

One problem that was identified with IPL treatment of Si-Ge nanocrystal films is that the film density after sintering is still relatively poor. In order to overcome this problem, we recently modified our deposition procedure in that Si-Ge nanocrystals are now co-deposited with an amorphous Si-Ge films. Rutherford backscattering measurements of these materials indicate that the porosity has been reduced to less than 10%, which is the level of accuracy of this technique. These amorphous/nanocrystalline (a/nc) films were crystallized by thermal annealing using the new furnace in Professor **Kortshagen**'s lab. Initial measurements of the electrical conductivity of 5% B-doped $Si_{80}Ge_{20}$ films were very promising (σ = 240.38 S/cm). Thermal conductivity of these samples is under evaluation by Professor **Wang**'s group.

Due to these highly promising results, the study of the crystallization of a/nc films will be continued in the next period. We will also continue the collaboration with Professor Gupta's group at the University of Virginia on laser-sintering of the Si-Ge nanocrystals. Furthermore, we will be focusing on TE development as described in **Activity 3** while continuing our investigation on material optimization. Figure of merit (ZT) of TE devices will be calculated based on the final electrical conductivity, Seebeck coefficient, and thermal conductivity measurements.

Activity Status as of January 1, 2019: As of January 1, 2019, the focus of the project is mainly on **Activity 3**.

Final Report Summary:

Performance of laser sintered phosphorous (P)-doped silicon-germanium films has been optimized by measuring their thermoelectric properties. The thermoelectric figure-of-merit ($ZT = S^2\sigma T/k$) was calculated by the conductivity and thermopower measurements at different temperatures from room temperature up to 873 K. The dark conductivity and Seebeck coefficient were measured in a vacuum chamber in the laboratory of Professor James Kakalios **(Figure 5 (section IX))**, a close collaborator at the University of Minnesota. The thermal conductivity is obtained by the ultrafast laser pump-probe technique, a method used by Prof. **Wang**.

In order to study the structural properties and understand the theory behind the changes in SiGe films with different deposition conditions, several characterization methods have been acquired; X-Ray Diffraction (XRD) and Atomic Force Microscopy (AFM) reveal the grain size of the sintered films. Raman spectroscopy shows the crystallinity of the initial and sintered thin films. Profilometry, ellipsometry, and Rutherford Backscattering Spectrometry (RBS) can be used to find the porosity and thickness of the films. X-Ray Photoelectron Spectroscopy (XPS) shows the accurate alloy ratio of Si/Ge while backscattering Scanning Electron Microscopy (SEM) can reveal the exact location of the incorporated Si and Ge phases before and after sintering. All the above-mentioned techniques have been used by Professor **Kortshagen**'s group, using the facilities available at the University of Minnesota Materials Characterization Facility.

Different dopant levels and alloy ratios have been studied to tune the carrier concentration of P-doped SiGe films, which is a significantly important factor in thermoelectrics. Also, the laser peak energy, scanning speed, and the pulse repetition rate (PRR) were optimized to maximize the figure of merit (ZT). Good film properties were found for intermediate powers and pulse frequencies. Under these conditions, the germanium rich regions produced a relatively uniform network of conductive pathways. For best results, hydrogen-terminated $Si_{80}Ge_{20}$ nanocrystals with 5% nominal phosphorous doping were sintered by a quasi-continuous wave (QCW) laser with a 1070 nm wavelength, Gaussian profile and pulse duration of 0.1 ms. The peak power of the laser was 1500 W at a 100% set point, and PRR was between 100 Hz and 1000 Hz. At room temperature, the best electrical conductivity achieved was 16.1 S/cm, the lowest thermal conductivity was 0.84 W/m-K, and the Seebeck coefficient was 144.9 μV/K.

ACTIVITY 3:
Description: TE Device Development

Thermoelectric efficiency is assessed by maximizing the figure of merit, $ZT = S^2\sigma T/k$. The Seebeck coefficient (S) assesses a material's ability to turn a temperature difference into an electrical current. Electrical conductivity (σ) must remain high, and the thermal conductivity (k) must be low for a high figure of merit. Measurements of the Seebeck coefficient will be performed with an experimental system available in the laboratory of Professor James Kakalios in the School of Physics and Astronomy. The electrical conductivity will be characterized with a device to be produced in **Activity 3**. This device will measure the voltage drop cross the TE material for a given electrical current passing through the device. The results from these electrical test devices and the characterization results of thermal properties described in activity 2, we will be able to determine the ZT figure of merit for the TE materials and assess efficiency.

Ultimately, the produced TE materials need to be tested in full TE modules, such as those schematically shown in Figure 1. This requires consideration of additional factors such as the thermal stability of the material and the reliability and robustness under thermal stress of the electrical contact(s) in the completed device. Tungsten will be tested as a good choice for an electrical contact material. Device characterization will involve exposing these devices to a temperature gradient and evaluating the electrical power generated.

Summary Budget Information for Activity 3: **ENRTF Budget: $ 122,401**
Amount Spent: $ 122,401
Balance: $ 0

Outcome	**Completion Date**
1. Develop TE test devices and energy generators from optimized materials	Dec. 31, 2018
2. Characterize device efficiencies	June 30, 2019

Activity Status as of January 1, 2017: Activity 3 will start after the completion of Activities 1 and 2. There is nothing yet to report.

Activity Status as of July 1, 2017: Activity 3 will start after the completion of Activities 1 and 2. There is nothing yet to report.

Activity Status as of January 1, 2018: Activity 3 will start after the completion of Activities 1 and 2. There is nothing yet to report.

Activity Status as of July 1, 2018: Activity 3 will start after the completion of Activities 1 and 2. There is nothing yet to report.

Activity Status as of January 1, 2019:

In this project period, we have focused on fabricating thermoelectric devices from Si-Ge thin films produced via two methods that have been identified as highly promising in the previous activities: 1) laser-sintering of nanoparticle films and 2) thermal sintering of amorphous/nanocrystalline mixed-phase materials.

Our studies of laser-sintered Si-Ge nanoparticle films has focused assessing the high-temperature thermoelectric properties of the films. Si-Ge will likely be the preferred material for high temperature applications, but in previous work we had only been able to assess the properties at room temperature. In our recent studies, we measured the Seebeck coefficient and electrical conductivity up to temperatures of 873 Kelvin, and the thermal conductivity up to 573K. From room temperature up to 573K, the thermal conductivity remained essentially constant, which enabled us to estimate the figure of merit ZT up to 873K. We showed that the Seebeck coefficient of the laser sintered thin films of phosphorous (P)-doped $Si_{80}Ge_{20}$ nanoparticles increases from -144.9 μV/K at room temperature to -390.1 μV/K at 873 K. The electrical conductivity increases from 16.1 S/cm at room temperature to 62.1 S/cm at 873 K and demonstrates an opposite trend when compared to bulk nanostructured materials. The thermal conductivity from room temperature to 573 K is essentially constant within the measurement error of our system at ~1.35 W/m-K. Therefore, if the thermal conductivity follows a similar temperature dependent trend as reported in past scientific literature, the figure of merit of the thin film $Si_{80}Ge_{20}$ is estimated to be 0.60 at 873 K which is comparable to a value of ~1 for bulk nanostructured materials. This result indicates that thin film P-doped SiGe can provide comparable performance with bulk nanostructured SiGe materials by using nanoparticle laser sintering as an easier, faster, and more cost-effective processing method.

In a second approach, we deposited thin films of p-type boron doped amorphous/nanocrystalline SiGe on quartz substrates via Plasma Enhanced Chemical Vapor Deposition (PECVD). The plasma uses RF powers of 1-10 W with pressures of 220-400 mTorr. The substrate is heated to 250°C during the film growth, which improves the quality of the film by providing the atoms with sufficient mobility to find a more stable and lower defect configuration. Boron is used as the dopant with concentrations ranging from 0.5% to 15%. Post deposition, polycrystalline structure is obtained by thermal annealing of the samples at 650°C for 10 hours. This method has been found to yield promising results, since the PECVD approach enables great control of the materials structure. We have found that the Seebeck coefficient can be increased by modulating the film growth between undoped and doped layers, an approach called modulation doping. The further evaluation of this approach is in progress.

Final Report Summary:

The main characteristic of SiGe films is their performance at high temperatures. Therefore, thermoelectric measurements of P-doped SiGe films have been done at temperatures up to 873 K. At the highest temperature, the electrical conductivity increases to 62.1 S/cm while the Seebeck coefficient increases to 390.1 μV/K. The thermal conductivity from room temperature to 573 K is essentially constant within the measurement error of our system at ~1.35 W/m-K. Therefore, if the thermal conductivity follows a similar temperature dependent trend, the figure of merit of the thin film $Si_{80}Ge_{20}$ is estimated to be 0.60 at 873 K which is comparable to a value of ~1 for bulk nanostructured materials. This result indicates that laser sintering, which provides a fast, easier, and more cost-effective way to produce thin film SiGe thermoelectric materials, can provide performance comparable with bulk nanostructured SiGe at high temperatures.

In order to produce films with less porosity, a second plasma reactor was used to study boron (B)-doped SiGe thin films. In this deposition procedure, SiGe nanocrystals are now co-deposited with an amorphous SiGe film. These amorphous/nanocrystalline (a/nc) films were crystallized by thermal annealing using a furnace in Professor **Kortshagen**'s lab. The effect of varying doping level, RF plasma power, alloy ratio, and annealing temperature on figure of merit of thin films was studied. The power factor was found to be highly dependent on the doping concentration with a peak at the mid-range doping concentration. This is mainly due the balance of the carrier density and carrier mobility in doped samples. Characterizations were performed at two points in the process, pre- and post-annealing. Results showed a minimum of three orders of magnitude improvement of the thermoelectric figure-of-merit after annealing in all conditions.

Best results are achieved by deposition of 6% boron doped $Si_{80}Ge_{20}$ thin films with RF plasma power of 4W while the substrate is heated to 250°C during the film growth. Rutherford backscattering measurements of these materials indicate that the porosity has been reduced to less than 10%, which is the level of accuracy of this technique. Annealing temperature and duration are correlated in producing fully polycrystalline samples. Thermal sintering at 1000°C for 1 hour produced samples with highest performance. The figure of merit of the polycrystalline samples at room temperature is 0.014 and increases to 0.035 at 450 K, which is comparable to the results reported in past scientific literature (0.01-0.04). At 450 K, the electrical conductivity is 150 S/cm, the Seebeck coefficient is 72 μV/K, and the thermal conductivity is ~ 1 W/m-K.

V. DISSEMINATION:
Description:

Professors **Kortshagen** and **Wang** are active members of their scientific communities. As such, they routinely disseminate results of their research through the publication of peer-reviewed research papers in scientific journals, conference papers and presentations, and seminar presentations at other universities and companies.

The characterization techniques previously discussed will provide a wealth of data in many custom formats for each application. In general, computer data will be stored both in custom format as well as in a universal form that does not require specific software for access. Microscopy images and analyzed or graphed data will be generated. Methods and conditions used for synthesizing and characterizing the samples will be recorded by the student researchers in the form of handwritten or electronic laboratory notebook entries.

Access to the data will be provided, upon request to the project director, within a reasonable period of time after collection. Data and laboratory notebooks will be maintained and stored for at least 3 years beyond the project end date, or 3 years following publication, whichever date is later.

The proposed project does not involve intellectual property rights at the moment. However, if an invention or proprietary discovery arises from the project and involves the stored data, the data will be made accessible to interested parties only after the intellectual property has been legally protected and conditions of the property rights are satisfied. The data collected and managed for this project is also subject to the data management and intellectual property policies established by the University of Minnesota.

Status as of January 1, 2017:

Research under this project has just begun, and the project investigators are working towards some first publications. We expect to report more dissemination results in the coming project periods.

Status as of July 1, 2017: Research under this project has made good progress, and the project investigators are working currently finalizing a manuscript reporting the results of the proposed Si-Ge from the first two project periods. We expect this manuscript to be submitted for publication the next few months.

Initial thermal measurement results of references samples have contributed to two journal publications: one published on *Nanoscale and Microscale Thermophysical Engineering* and one just accepted by *Frontiers in Energy* as an invited article for a special issue on **Energy Materials** (solid-state energy conversion enabled by TE devices). The LCCMR grant has been acknowledged in both papers for partially supporting a research assistant to conduct the research work. The preliminary results of the thermal conductivity of nano-porous indium gallium nitride will also be presented at the *36th International Thermoelectric Conference* (ICT 2017) in Pasadena/California from July 31, 2017 to August 03, 2017.

Status as of January 1, 2018: The invited paper by *Frontiers in Energy*, which is based on the preliminary data of thermal measurements on reference samples, has been published online. This serves as an ideal platform to advertise our work supported by the LCCMR grant.

Another paper, reporting the results of laser-sintered SiGe particles was recently submitted and has recently been published:

Xie, K., Mork, K., Held, J. T., Mkhoyan, K. A., Kortshagen, U., & Gupta, M. C. (2018). Quasi continuous wave laser sintering of Si-Ge nanoparticles for thermoelectrics. Journal of Applied Physics, 123(9). https://doi.org/10.1063/1.5018337

A second paper is in preparation.

Status as of July 1, 2018: A paper presenting the thermoelectric properties of laser sintered doped Si-Ge films at high temperatures is under preparation:

High Temperature Thermoelectric Properties of Laser Sintered Thin Films of Si-Ge Nanoparticles (in progress), Xie, K., Mork, K., Kortshagen, U., & Gupta, M. C.

Status as of January 1, 2019:

The new paper has been published:
High Temperature Thermoelectric Properties of Laser Sintered Thin Films of phosphorous-doped Si-Ge Nanoparticles, Xie, K., Mork, K., Kortshagen, U., & Gupta, M. C., AIP Advances 9(1), 015227, https://doi.org/10.1063/1.5085016

Final Report Summary:

The LCCMR grant has been acknowledged in four journal publications as well as two conference presentations. The first two papers presented the thermoelectric properties of laser sintered doped Si-Ge films at room and high temperatures. The other four papers presented the initial thermal measurement results of reference samples and ultrafast-laser based metrology development related with this project. Also, the team has one collaborative paper on nanoparticles as potential TE materials currently under review. In addition, the team has produced a number of oral presentations at both professional conferences and industrial workshops, which greatly facilitates the broader dissemination of the results for ultrafast laser pump-probe technique for thermal characterization of TE materials with micro/ nanostructures as well as the results for thermal sintering of doped Si-Ge thin films.

Journal Papers:
[1] Quasi continuous wave laser sintering of Si-Ge nanoparticles for thermoelectrics, Xie, K., Mork, K., Held, J. T., Mkhoyan, K. A., Kortshagen, U., Gupta, M. C., Journal of Applied Physics, 2018, 123(9), 094301. https://doi.org/10.1063/1.5018337

[2] High Temperature Thermoelectric Properties of Laser Sintered Thin Films of phosphorous-doped Si-Ge Nanoparticles, Xie, K., Mork, K., Kortshagen, U., Gupta, M. C., AIP Advances, 2019, 9(1), 015227. https://doi.org/10.1063/1.5085016

[3] The Ultrafast Laser Pump-probe Technique for Thermal Characterization of Materials with Micro/ nanostructures, Zhu, J., Wu, X.W, Lattery, D.M., Zheng, W., Wang, X.J, Nanoscale and Microscale Thermophysical Engineering, 2017, 21(3), 177-198.
http://dx.doi.org/10.1080/15567265.2017.1313343

[4] Largely reduced cross-plane thermal conductivity of nanoporous $In_{0.1}Ga_{0.9}N$ thin films directly grown by metal organic chemical vapor deposition, Xu, D., Wang, Q., Wu, X. *et al.* Frontiers in Energy, 2018, 12(1), 127-136.
https://doi-org.ezp2.lib.umn.edu/10.1007/s11708-018-0519-5

[5] Properties of Anisotropic Nanoarrays with Polarization Coupling, Lattery, D., Choi, J, Kim, M, Lee, B.J., and Wang, X.J., 2018, Scientific Reports, 8, p. 13896.
https://www.nature.com/articles/s41598-018-32265-w

[6] A Modified Theoretical Model to Predict the Thermal Interface Conductance Considering Interface Roughness, Zhang, Y. Y, Ma, D.K., Zang, Y., Wang, X.J., Yang, N., 2018, Frontiers in Energy, 6, p. 48.
https://www.frontiersin.org/articles/10.3389/fenrg.2018.00048/full

[7] Thermal Transport in ZnO Nanocrystal Networks Synthesized by Nonthermal Plasma, Wu, X.W., Greenberg, B.L., Zhang, Y.Y., Aydil, E.S., Kortshagen, U., Wang, X.J. (submitted)

Conferences:
[1] The *36th International Thermoelectric Conference* (ICT), in Pasadena/California, July 31-August 03 (2017).

[2] Invited talk at the 3M Corporate Headquarters, in Maplewood/Minnesota, March (2018).

[3] The 60th *Electronic Materials Conference* (EMC) under *Materials Research Society* (MRS), in Santa Barbara/California, June 24-29 (2018).

[4] *International Mechanical Engineering Congress & Exposition* (IMECE) under the *American Society of Mechanical Engineers* (ASME), in Pittsburgh/Pennsylvania, November 9-15 (2018).

[5] *Materials Research Society* (MRS) Meeting and Exhibit, in Phoenix/Arizona, April 22-26 (2019).

VI. PROJECT BUDGET SUMMARY:

A. ENRTF Budget Overview:

Budget Category	$ Amount	Overview Explanation
TOTAL ENRTF BUDGET:	**$400,000**	

Please see attached amended budget worksheet

Explanation of Use of Classified Staff: N/A

Explanation of Capital Expenditures Greater Than $5,000:

We have requested funding to purchase a hydraulic hot-pressing system from the MTI Corporation as part of the project budget ($23,120). This hot-pressing system is crucial for thermal sintering of the Si-Ge nanoparticles to form high-quality and high-performance TE materials. We present below the equipment specifications:

The MTI hot press model OTF-1200X-VHP4 is capable of going up to 1100^{o}C (temperature) and 10 MPa (pressure). Beyond this, it has a split vertical tube furnace consisting of a vacuum-sealed 4" quartz tube, which allows for operation under vacuum or in an inert gas environment. This system is equipped with a 30-segment programmable temperature controller and an auto tune PID for over-heating protection, which allows for precise control of temperature for the thermal sintering of TE materials.

Number of Full-time Equivalents (FTE) Directly Funded with this ENRTF Appropriation: 1.1 FTEs

Number of Full-time Equivalents (FTE) Estimated to Be Funded through Contracts with this ENRTF Appropriation: 0

B. Other Funds:

Source of Funds	$ Amount Proposed	$ Amount Spent	Use of Other Funds
Non-state			
	$226,296	$~226,296	Preliminary research funded under a project by the National Science Foundation. Funds under this project have been expended.
State			
	$0	$0	
TOTAL OTHER FUNDS:	**$**	**$**	

VII. PROJECT STRATEGY:

A. Project Partners:

Professor Xiaojia **Wang** is an expert in analyzing the thermal properties of materials. As a junior faculty member, she has published 14 journal articles in the area of micro-nanoscale thermal transport. Her time-domain thermoreflectance system is equaled only by a few similar systems in the country. Professor **Kortshagen** brings unique expertise in materials synthesis and electrical characterization. Since joining the University of Minnesota in 1996, he has directed research on grants exceeding $25M, including large research groups around nanograin materials, which has led to over 100 research papers, three patents and two technology licenses to DuPont-Innovalight and Dow Corning.

Professor Kortshagen is the Project Director of this proposed work, and he will be responsible for the overall management of this project and the status reports of project update. For this project, he will be working on the synthesis of silicon-germanium nanoparticles with precisely controlled sizes and doping levels. In addition, he will characterize the electrical properties of scalable thermoelectric materials from thermal sintering of nanoparticles. **Xiaojia Wang's** expertise lies in the heat transfer in micro- and nano-scale using novel ultrafast optical characterization techniques. She will be in charge of the thermal sintering of nanoparticles, and she will also investigate the thermal properties of the proposed thermoelectric materials and correlate the material thermoelectric performance to their property characterization. The two principal investigators will coordinate with each other to experimentally develop and characterize thermoelectric test devices and energy generators.

B. Project Impact and Long-term Strategy:

This proposed work aims at improving the energy conversion efficiency of thermoelectric devices, and subsequently reduce the usage of fossil fuels to ameliorate air pollution and the emission of greenhouse gases. It leverages upon research that is performed by the "Sustainable Nanocrystal Materials" group (directed by **Kortshagen**) of the National Science Foundation-funded University of Minnesota Materials Research Science and Engineering Center. If successful, the outcomes of this work will contribute to the scientific knowledge base, but also hold great prospect for commercialization.

The project team also has a strong track record in technology transfer from academic labs to industry. The nanocrystal plasma synthesis process developed in **Kortshagen**'s lab has been patented and was exclusively licensed to Innovalight, Inc. (acquired by DuPont) and Dow Corning. The project team is interested in continuing this proactive interaction with industry in order to translate any outcomes of the proposed research quickly into industry and to help build a viable national industry in the renewable energy area.

C. Funding History:

Funding Source and Use of Funds	Funding Timeframe	$ Amount
National Science Foundation	8/15/2014-8/14/2017	$226,296
		$
		$

VIII. FEE TITLE ACQUISITION/CONSERVATION EASEMENT/RESTORATION REQUIREMENTS:

N/A

IX. VISUAL COMPONENT or MAP(S):

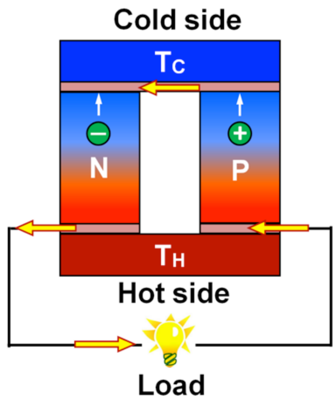

Figure 1: Schematic of a thermoelectric energy generator.

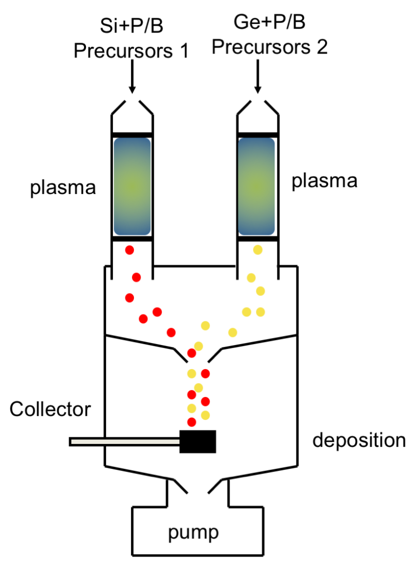

Figure 2: Schematic of the plasma deposition reactor to be constructed.

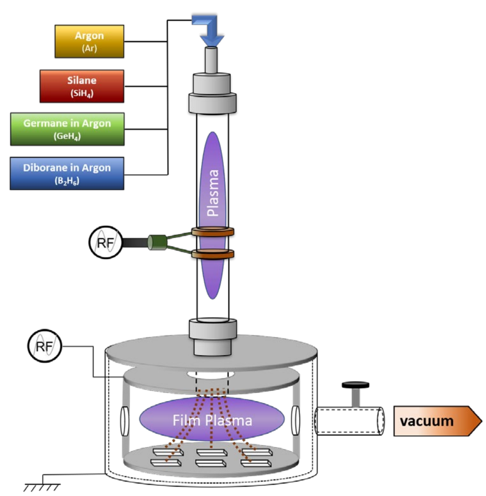

Figure 3: Schematic of the dual plasma co-deposition reactor for amorphous/nanocrystal film fabrication.

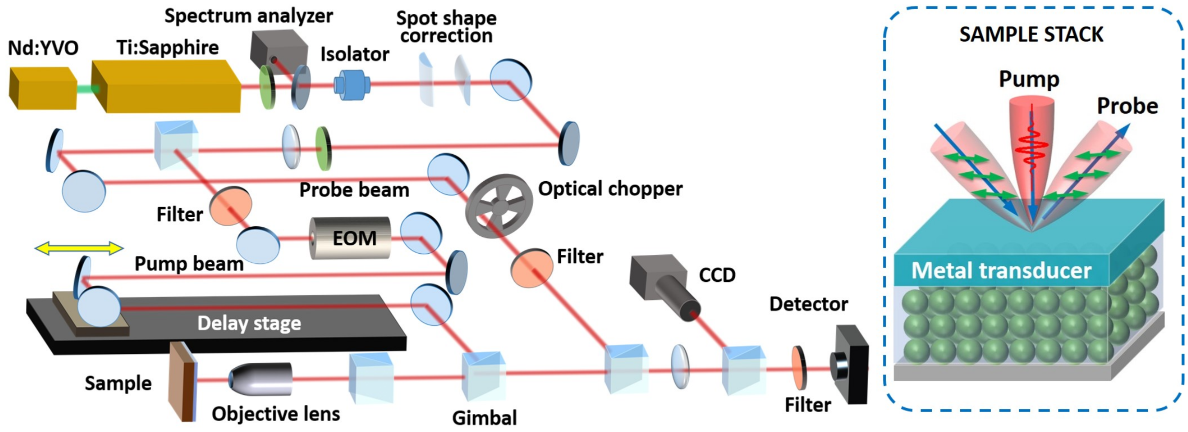

Figure 4: Schematic of the custom-built ultrafast pump-probe system and the Si-Ge sample stack for thermal measurements.

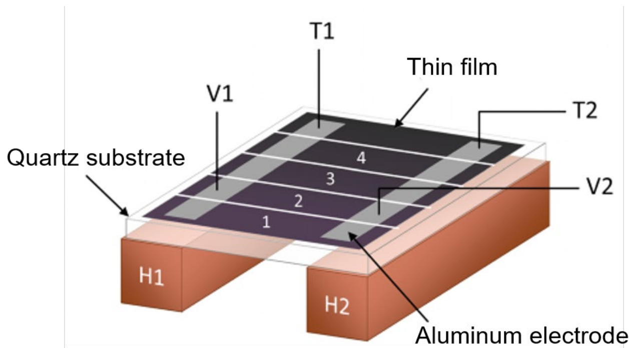

Figure 5: Schematic of the thermopower measurement system.

X. RESEARCH ADDENDUM:

N/A, see email from Michael McDonough from Nov. 23, 2015

XI. REPORTING REQUIREMENTS:
Periodic work plan status update reports will be submitted no later than January 1, 2017, July 1, 2017, January 1, 2018, July 1, 2018, and January 1, 2019. A final report and associated products will be submitted between June 30 and August 15, 2019.

Environment and Natural Resources Trust Fund
M.L. 2016 Project Budget

Project Title: Waste Heat Recovery with Efficient Thermoelectric Energy Generators
Legal Citation: M.L. 2016, Chp. 186, Sec. 2, Subd. 07b
Project Manager: Uwe Kortshagen
Organization: University of Minnesota
M.L. 2016 ENRTF Appropriation: $ 400,000
Project Length and Completion Date: 3 Years, June 30, 2019
Date of Report: Sep. 26, 2019

ENVIRONMENT AND NATURAL RESOURCES TRUST FUND BUDGET	Activity 1 Budget	Amount Spent	Activity 1 Balance	Activity 2 Budget	Amount Spent	Activity 2 Balance	Revised Activity 3 Budget 9/26/19	Amount Spent	Activity 3 Balance	Revised TOTAL BUDGET 9/26/19	TOTAL SPENT	TOTAL BALANCE
BUDGET ITEM	***Fill in your activity title here.***			***Fill in your activity title here.***								
Personnel (Wages and Benefits)	$145,410		$0	$100,000		$0	$113,487		$0	$358,897	$358,896	$0
Uwe Kortshagen, PI: $11,879 (75% salary, 25% benefits); 5% FTE each year for 3 years, 3% increase years 2-3		$13,638			$13,376			$25,953				
Xiaojia Wang, Co-PI: $6,458 (75% salary, 25% benefits): 5% FTE each year for 3 years, 3% increase years 2-3		$6,676			$6,897			$10,765				
2 RA's at 50%: $91,372 (58% salary, 24% benefits); 50% FTE each year for 3 years, 3% increase years 2-3		$125,096			$79,727			$76,769				
Equipment/Tools/Supplies	$1,557		$0	$1,100		$0	$1,100		$0	$3,757	$3,757	$0
Sample holder for thermal sintering: 1/2" graphite die with an operation temperature of 400 Celsius in air and > 400 Celsius under nitrogen inert environment ($200)		$0										
Equipment and supplies to construct a reactor for nanoparticle synthesis, including RF power supplies ($6000), 2 matchboxes ($100*2 = $200), 1 mass flow controller ($1500) and 1 readout ($2000), 1 pressure gauge ($600) and 1 readout($500), 2 pneumatic valves ($450*2=$900), 2 ball valves ($100*2=$200), 2 vacuum right-angle valves ($300*2=$600) 2 ultra-torr to KF40 adapters ($50*2=$100), 2 quartz reactor tubes ($40*2=$80), 1 wye tee ($1000), other accessories (lines, fittings, welding, $3000)		$1,557			$1,100			$1,100				
Cost for purchasing precursor gases ($400*3=$1200), sample substrates ($100*3=$300), and chemicals ($100*3=$300) for nanoparticle synthesis		$0										
Purchasing reference materials, including bare silicon ($3*150), silicon dioxide ($3*150), sapphire ($3*200) wafers for thermal characterization.		$0										
Capital Expenditures Over $5,000	$0		$0	$0		$0	$0		$0	$0	$0	$0
Equipment and supplies to construct a mechanical hot-pressing system to sintering thermoelectric modules, including an integrated vacuum heated pressing furnace up to 1100 Celsius with 4" quartz tube and water cold flange (OTF-1200X-VHP4, $23,120)		$0										
Other	$10,734		$0	$18,798		$0	$7,814		$0	$37,346	$37,346	$0
User fees for rental and usage of facilities at the campus CharFac center for sample thermal property characterization (electrical conductivity, ellipsometry, and atomic force microscopy) and for nanoparticle structural/property characterization (X-ray diffraction, secondary electron microscopy, Raman spectroscopy, tunneling electron microscopy, and ellipsometry) (3*$3293=$9879)		$10,734			$18,798			$7,814				
Usage fees for the MNC Facility for housing the plasma reactor and precursor gases and processing samples ($2000*3=$6000)		$0										
MNC Facility Fees for thin-film deposition of metal transducers (sputtering and thermal evaporation, ($1500*3=$4500)		$0										
COLUMN TOTAL	**$157,701**	**$157,701**	**$0**	**$119,898**	**$119,898**	**$0**	**$122,401**	**$122,401**	**$0**	**$400,000**	**$400,000**	**$0**