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

Date of Report: May 29, 2016

Date of Next Status Update Report: January 1, 2017

Date of Work Plan Approval: June 7, 2016

Project Completion Date: June 30, 2019

Does this submission include an amendment request? _NO_

PROJECT TITLE: Waste Heat Recovery with Efficient Thermoelectric Energy Generators

Project Manager: Uwe Kortshagen

Organization: University of Minnesota

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Location: Hennepin

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

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 green house 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 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:

Project Status as of July 1, 2017:

Project Status as of January 1, 2018:

Project Status as of July 1, 2018:

Project Status as of January 1, 2019:

Overall Project Outcomes and Results:

IV. PROJECT ACTIVITIES AND OUTCOMES:

ACTIVITY 1:
Description: Nanograined Materials Synthesis

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

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:	**$ 0**
Balance:	**$ 157,701**

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:

Activity Status as of July 1, 2017:

Activity Status as of January 1, 2018:

Activity Status as of July 1, 2018:

Activity Status as of January 1, 2019:

Final Report Summary:

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: **$ 0**
Balance: **$ 119,898**

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:

Activity Status as of July 1, 2017:

Activity Status as of January 1, 2018:

Activity Status as of July 1, 2018:

Activity Status as of January 1, 2019:

Final Report Summary:

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: **$ 0**
Balance: **$ 122,401**

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 Status as of July 1, 2017:

Activity Status as of January 1, 2018:

Activity Status as of July 1, 2018:

Activity Status as of January 1, 2019:

Final Report Summary:

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:

Status as of July 1, 2017:

Status as of January 1, 2018:

Status as of July 1, 2018:

Status as of January 1, 2019:

Final Report Summary:

VI. PROJECT BUDGET SUMMARY:

A. ENRTF Budget Overview:

Budget Category	$ Amount	Overview Explanation
Personnel:	$ 336,322	Project Manager (Prof. Kortshagen): $11,879 (75% salary, 25% benefits); 5% FTE each year for 3 years, 3% increase years 2-3 Co-Principal Investigator (Prof. Wang), $6,458 (75% salary, 25% benefits): 5% FTE each year for 3 years, 3% increase years 2-3 2 research assistants: $91,372 (58% salary, 24% benefits); 50% FTE each year for 3 years, 3% increase years 2-3
Equipment/Tools/Supplies:	$20,180	Budget for equipment and supplies to construct a reactor for particle synthesis, lab supplies, and user fees for rental and usage of facilities at the campus CharFac center 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) Cost for purchasing precursor gases ($400*3=$1200), sample substrates ($100*3=$300), and chemicals ($100*3=$300) for nanoparticle synthesis Purchasing reference materials, including bare silicon ($3*150), silicon dioxide ($3*150), sapphire ($3*200) wafers for thermal characterization.
Capital Expenditures over $5,000:	$23,120	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)
Other:	$20,378	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) ($3293*3) Usage fees for the MNC Facility for housing the plasma reactor and precursor gases and processing samples ($2000*3=$6000); and MNC Facility Fees for thin-film deposition of metal transducers (sputtering and thermal evaporation, $1500*3=$4.500)
TOTAL ENRTF BUDGET:	**$400,000**	

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	$~126,000	Preliminary research funded under a project by the National Science Foundation. On July 1, 2016, we estimate that ~$100k will be remaining to support this research project
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):

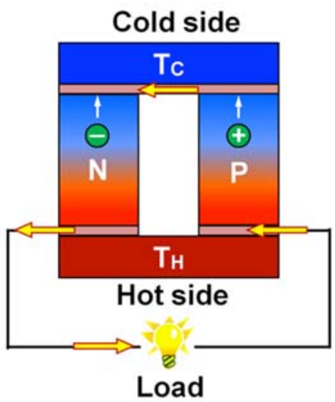

Figure 1: Schematic of a thermoelectric energy generator.

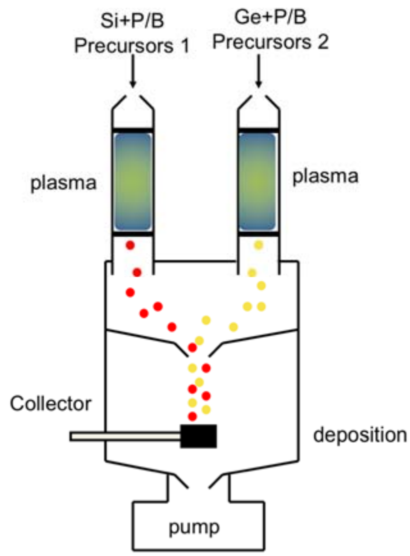

Figure 2: Schematic of the plasma deposition reactor to be constructed.

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: May 29, 2016

ENVIRONMENT AND NATURAL RESOURCES TRUST FUND BUDGET	Activity 1 Budget	Amount Spent	Activity 1 Balance	Activity 2 Budget	Amount Spent	Activity 2 Balance	Activity 3 Budget	Amount Spent	Activity 3 Balance	TOTAL BUDGET	TOTAL BALANCE
BUDGET ITEM	***Fill in your activity title here.***			***Fill in your activity title here.***			***Fill in your activity title here.***				
Personnel (Wages and Benefits)	$109,808		$109,808	$112,005		$112,005	$114,509		$114,509	$336,322	$336,322
Uwe Kortshagen, PI: $11,879 (75% salary, 25% benefits); 5% FTE each year for 3 years, 3% increase years 2-3											
Xiaojia Wang, Co-PI: $6,458 (75% salary, 25% benefits): 5% FTE each year for 3 years, 3% increase years 2-3											
2 RA's at 50%: $91,372 (58% salary, 24% benefits); 50% FTE each year for 3 years, 3% increase years 2-3											
Equipment/Tools/Supplies	$17,980		$17,980	$1,100		$1,100	$1,100		$1,100	$20,180	$20,180
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)											
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)											
Cost for purchasing precursor gases ($400*3=$1200), sample substrates ($100*3=$300), and chemicals ($100*3=$300) for nanoparticle synthesis											
Purchasing reference materials, including bare silicon ($3*150), silicon dioxide ($3*150), sapphire ($3*200) wafers for thermal characterization.											
Capital Expenditures Over $5,000	$23,120		$23,120	$0		$0	$0		$0	$23,120	$23,120
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)											
Other	$6,793		$6,793	$6,793		$6,793	$6,792		$6,792	$20,378	$20,378

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)											
Usage fees for the MNC Facility for housing the plasma reactor and precursor gases and processing samples ($2000*3=$6000)											
MNC Facility Fees for thin-film deposition of metal transducers (sputtering and thermal evaporation, ($1500*3=$4500)											
COLUMN TOTAL	**$157,701**	**$0**	**$157,701**	**$119,898**	**$0**	**$119,898**	**$122,401**	**$0**	**$122,401**	**$400,000**	**$400,000**