NSF/DOE Thermoelectric Partnership: Inorganic-Organic Hybrid Thermoelectrics

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ACE071

Overview

Timeline

- 01/01/2011
- 12/31/2013
- 10%

Budget

- Total project funding
  - DOE:$ 426,950
- Funding received in FY10
  - DOE:$ 141,757
- Funding for FY11
  - DOE:$ 137,550

Barriers

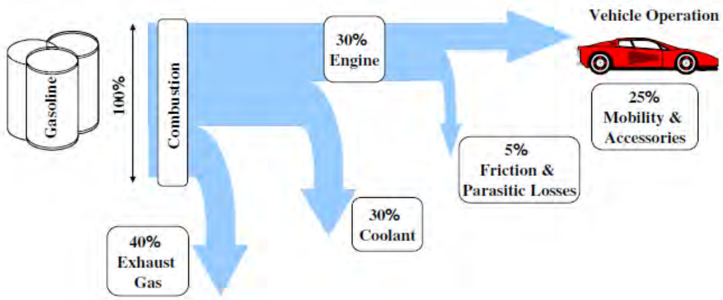
- Barriers addressed
  - MATERIALS: Bulk synthesis of inorganic quantum wires with diameters less than 5 nm.
  - INTERFACES: Large-scale assembly of inorganic nanowires with engineered interfaces that are electrical conductors and thermal insulators.
  - METROLOGY: Finding metals that have low contact resistance with the interface-engineered inorganic-organic hybrids.
- Ultimate Goal: Thermoelectric modules with zT>3 performance

Partners

- None

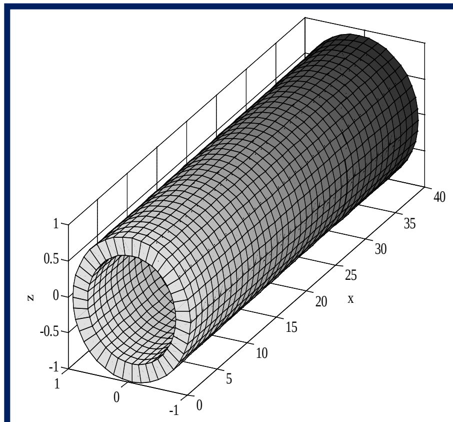
Objectives: Inorganic-Organic Hybrid Thermoelectrics

Ultimate Goal of this Project



- To recover waste heat from automobile exhausts through the fabrication of large area thermoelectric modules that exhibit zT>3 performance.

Pictorial Representation of a thermoelectric module



Objectives of this Project

- Barriers addressed
  - Bulk synthesis of inorganic quantum wires with ultra-small diameters (< 5 nm) of $CoSb_3$ and InSb for achieving zT>3 thermoelectric performance
  - Large-scale assembly of inorganic nanowires in an interface-engineered manner using conjugated organic molecular linkers and conducting polymer films into cm^2 sized thermoelectric devices that exhibit zT>3 performance
  - Deduction of the metal that has least contact resistance with the inorganic-organic hybrids for assembling thermoelectric devices into modules.

Milestones: Inorganic-Organic Hybrid Thermoelectrics

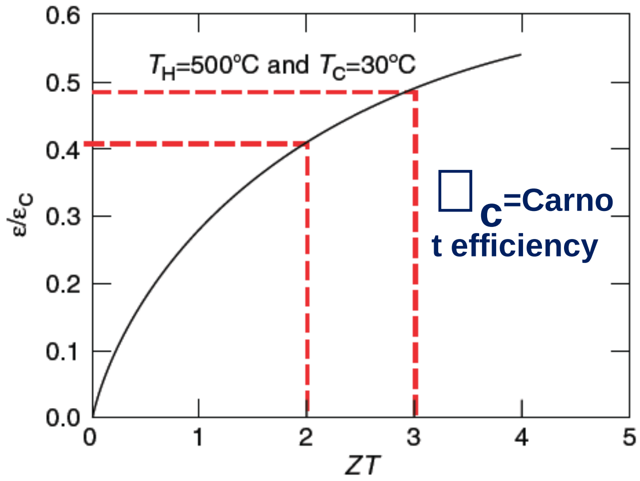
Month/Year	Milestone or Go/No-Go Decision
March 2011	• MILESTONE: Accomplished the synthesis of Zn_3P_2, InN and $CoSb_3$ nanowires using self-catalysis. • MILESTONE: In-situ functionalization of nanowires with conjugated linker molecules was accomplished. • GO/NO-GO DECISION: *Ex-situ* functionalization of nanowires is not as effective as *in-situ* functionalization and does not efficiently lead to covalent bond formation between nanowire surfaces and the conjugated linker molecules. • MILESTONE: Interface-engineered assembly of inorganic nanowires to each other through linker molecules was accomplished and the thermopower of the resulting pellet was successfully measured.

Approach: Tailored Synthesis and Assembly of Quantum wires

- Figure-of-merit for thermoelectrics, ZT, is

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

Seebeck coefficient (S), **Electrical conductivity** (σ), **Electronic thermal conductivity** (κ_e), **Lattice thermal conductivity** (κ_l)



- A large temperature difference, 800 °C, is available for power generation in vehicles.
- Both n-type and p-type materials with *ZT* ~3, with low contact resistances or losses, are necessary for efficiently converting waste heat from the exhaust into electricity.

- Matsubara and Matsuura, A Thermoelectric Application to Vehicles (Chapter 52), in Thermoelectrics Handbook: Macro to Nano, 2006.
- Tritt *et al*, MRS Bulletin, 33, 367, 2008.

Approach: Tailored Synthesis and Assembly of Quantum wires

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

- κ_e cannot be reduced without reducing σ (Wiedemann-Franz Law)
- ZT enhancement requires reduction in the κ_l of materials,

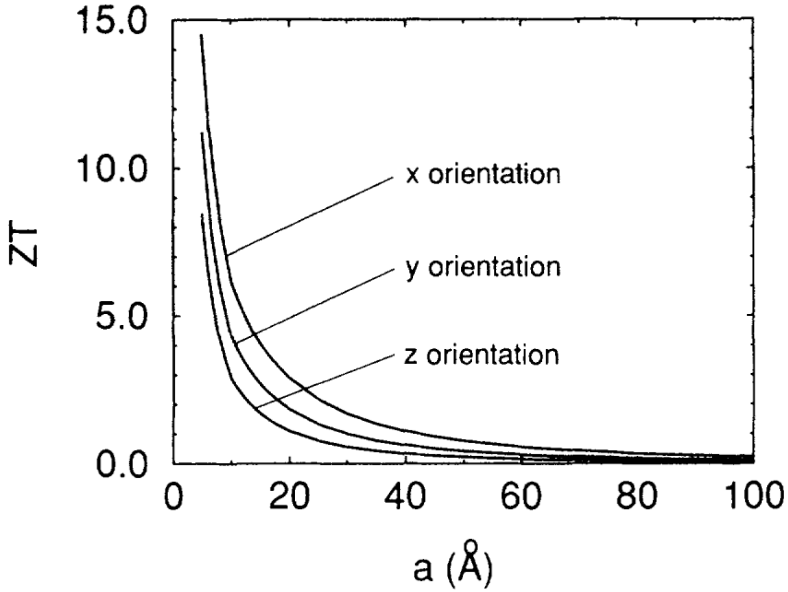
$$\kappa_l = \frac{1}{3} \int c_\lambda(\lambda, T)\, v(\lambda)\, L(\lambda, T)\, d\lambda$$

λ is the wavelength, c_λ is the spectral specific heat per unit wavelength, v is the group velocity, L is the spectral mean-free path.

- Theoretical predictions indicate that κ_l of materials could be reduced
  - either by a reduction in $c_\lambda(\lambda, T)\, \upsilon(\lambda)$ through phonon confinement in nanowires and superlattices with extremely small dimensions, or
  - by a reduction in $L(\lambda, T)$ through enhanced phonon scattering in boundaries and interfaces in nanowires and composites.

Approach: Strategy for Enhancing ZT

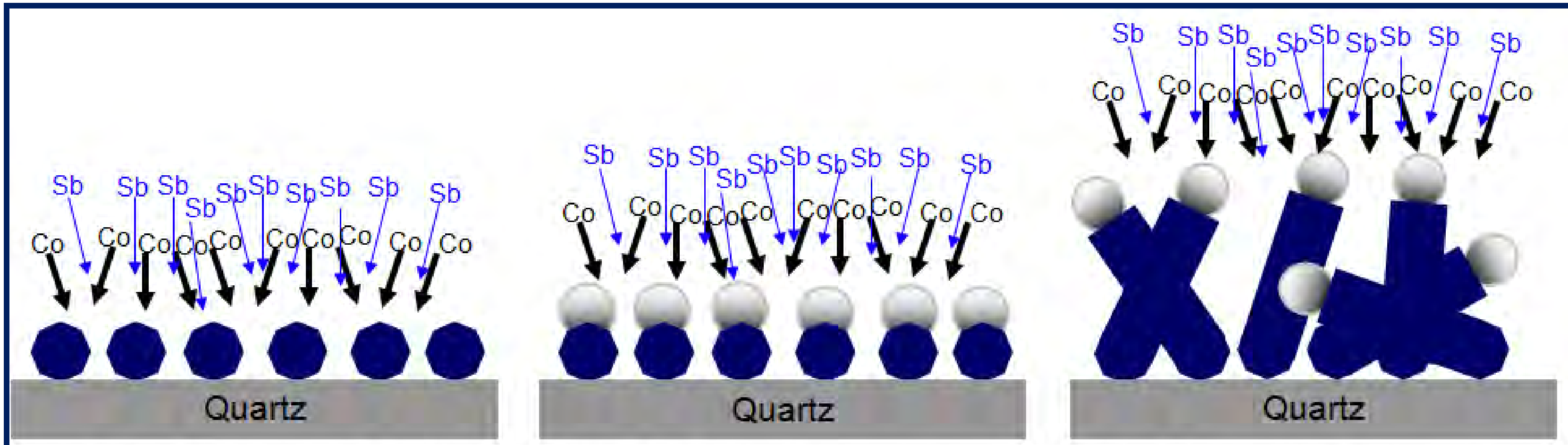
- Single-crystalline nanowires exhibit good electrical conductivity (*σ)* along their lengths.
- Lattice thermal conductivity in nanowires can be scaled to $(\text{diameter/roughness})^2$, and hence can be reduced through
  - a reduction in their diameters (to sub-5 nm length scales)
  - enhancing surface roughnesses



•How can the bulk synthesis of powders of nanowires with sub-5 nm diameters be accomplished in a pristine and contaminant-free manner? How can they be assembled on a large-scale in a reliable manner?

•Chen and Dames, Thermal Conductivity of Nanostructured Thermoelectric Materials. In Thermoelectrics Handbook, CRC Press, 2005.
•Martin *et al*, Phys. Rev. Lett., 102, 2009.
•Hicks and Dresselhaus, Physical Review B, 47, 16631, 1993.

Approach: Bulk Synthesis of Nanowires



STEP 1: Formation of $CoSb_3$ nuclei on the substrate

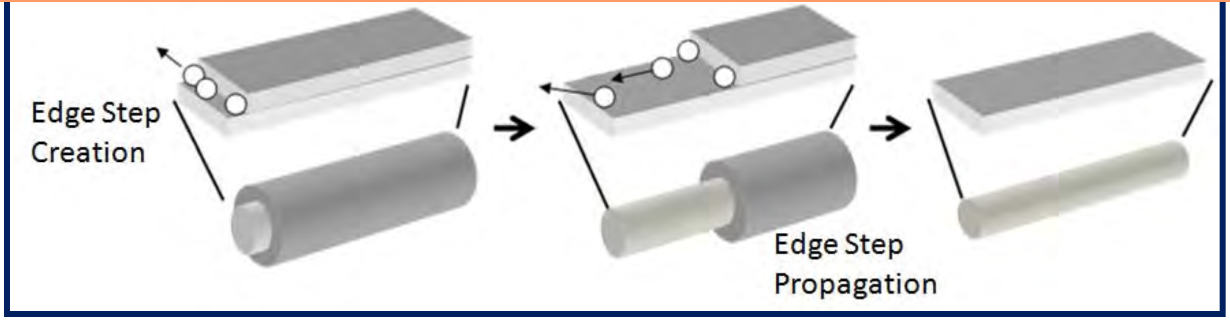
STEP 2: Selective wetting and antimony droplet formation on top of the $CoSb_3$ nuclei

STEP 3: Liquid phase epitaxy through the antimony droplet for $CoSb_3$ nanowire formation

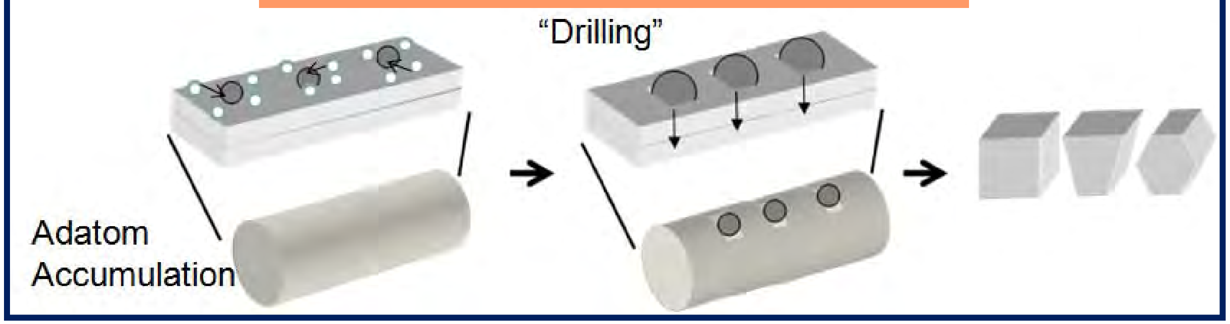
- Self-catalysis allows for the formation of nanowires devoid of any unintentional contaminants or dopants.
- Self-catalysis is scalable for the bulk production of nanowire/quantum wire powders
- Self-catalysis can be employed to obtain nanowires of any compound semiconductor (e.g., InSb, $CoSb_3$, Zn_3P_2)

Approach: Post-synthesis decomposition for Quantum Wires

Layer-by-layer Decomposition at Nanoscale

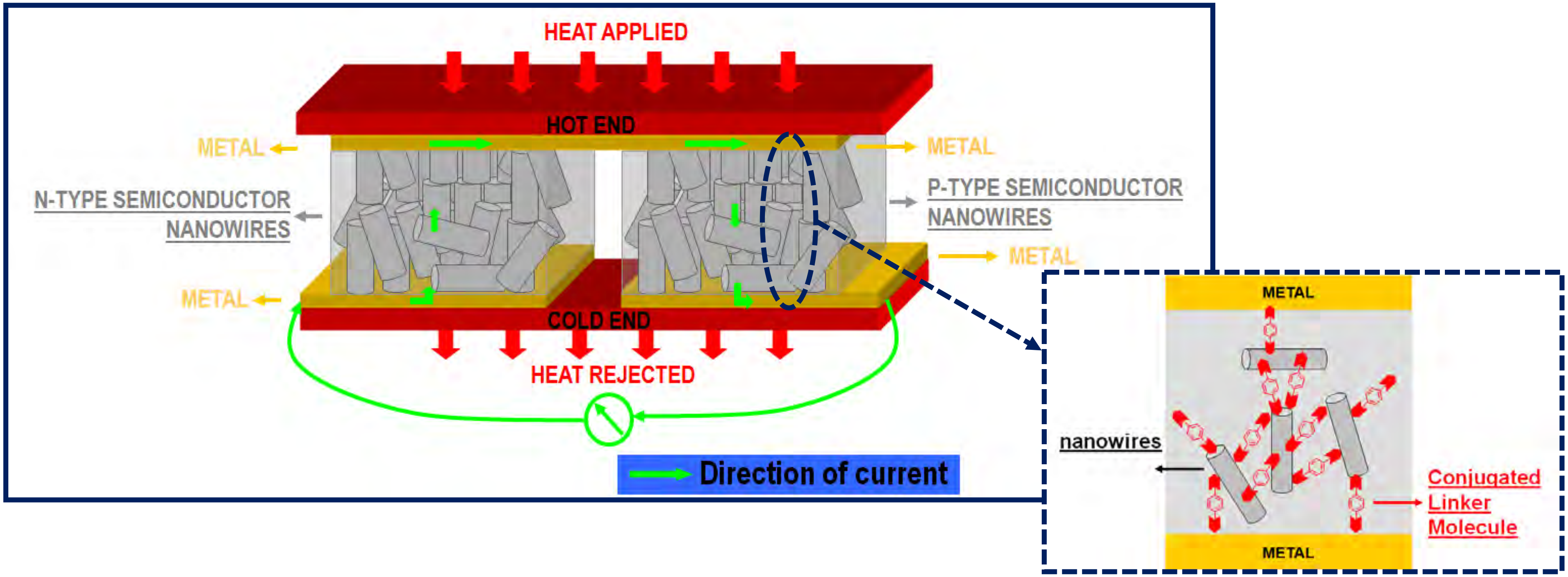


Bulk Decomposition



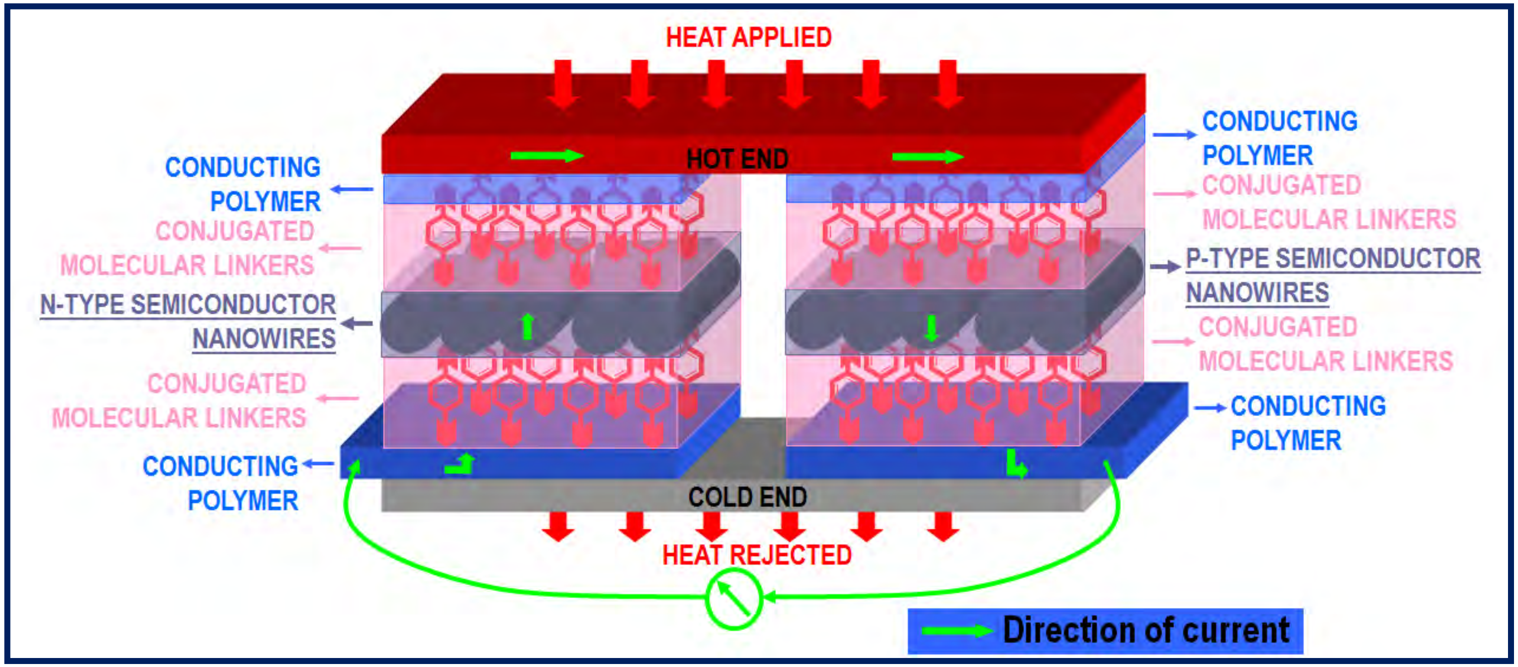
- Layer-by-layer decomposition, an exclusive nano-scale phenomenon, will allow for obtaining diameters less than 5 nm in quantum wires in a uniform and reproducible manner

Approach: Interface-Engineered Assembly of Quantum Wires I



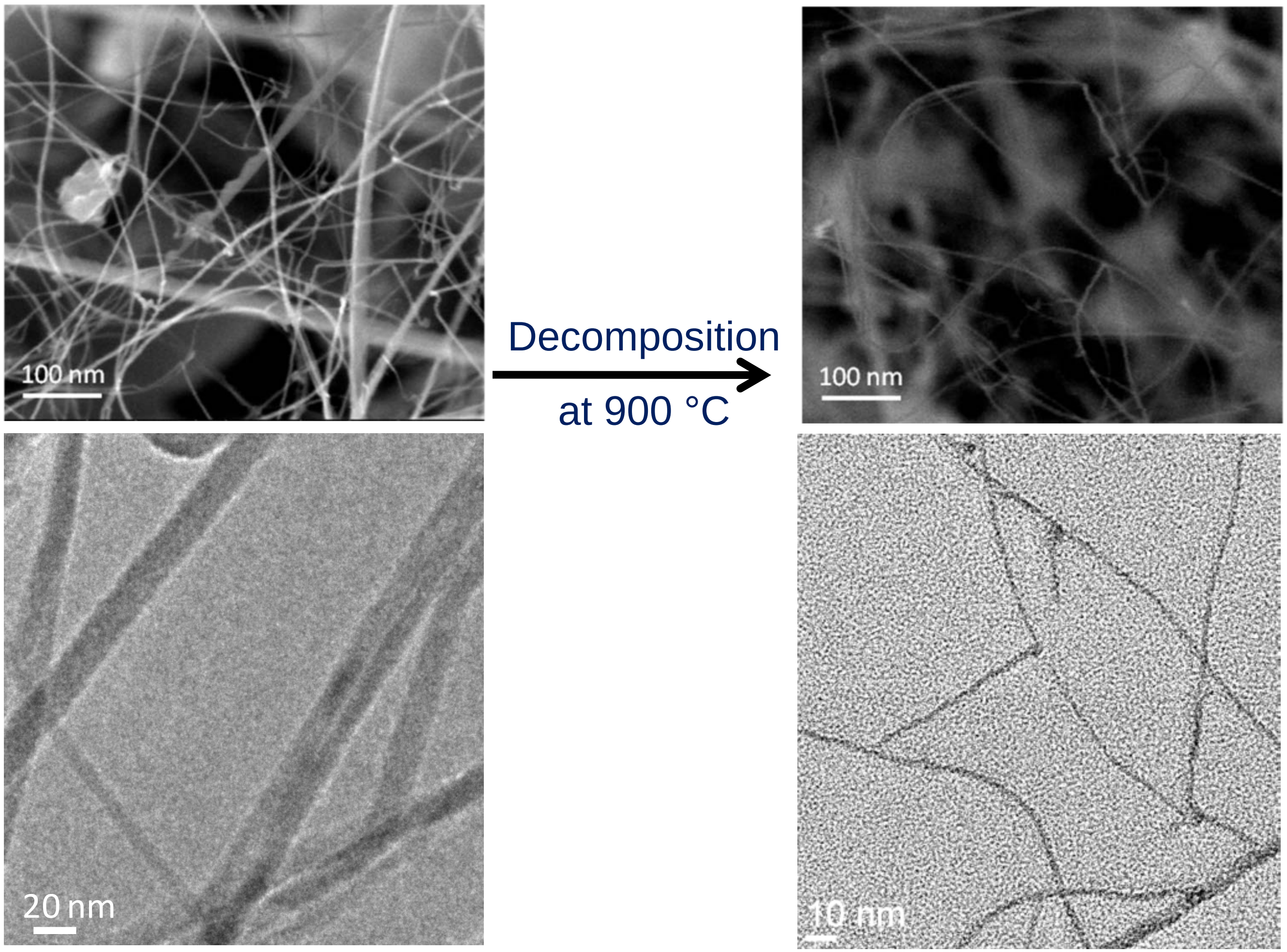
- “Molecular wiring” of nanowires to each other makes the nanowires pellets robust and delamination-free
- Chemistry of the “molecular wires” can be varied to tune the interfacial electrical and thermal transport .

Approach: Interface-Engineered Assembly of Quantum Wires II



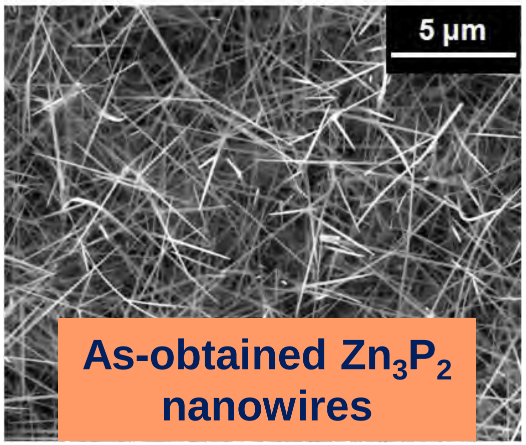
- Conducting polymer films form a uniform electrical contact between the nanowires.
- Interfacial electrical and thermal transport tunable through variations in the linker molecule and conducting polymer chemistries.

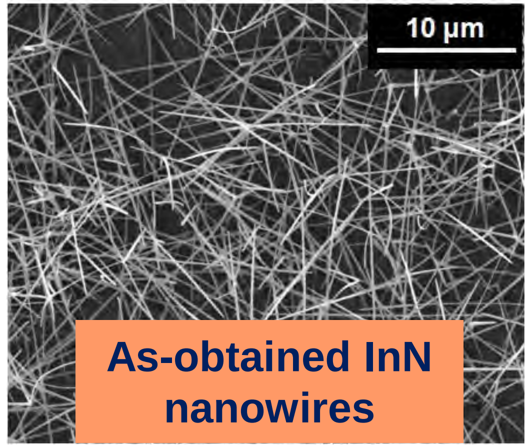
Technical Accomplishment: Synthesis of GaN Nanowires and quantum wires

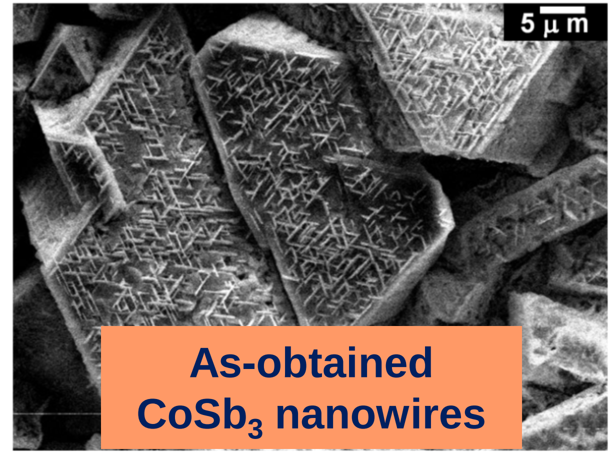


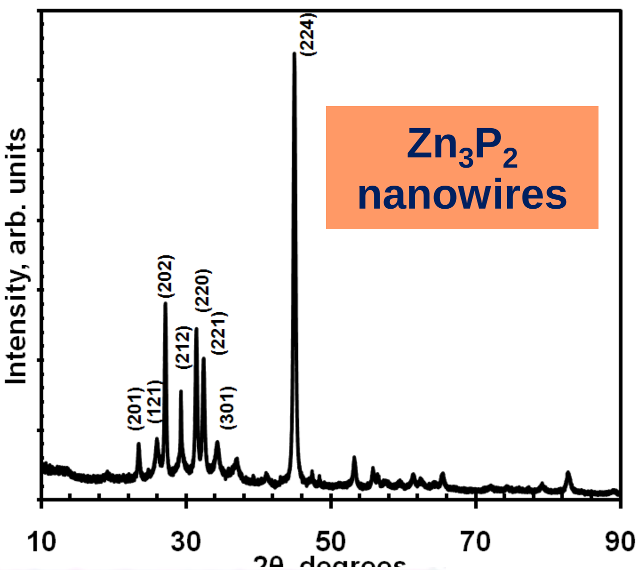
- Self-catalysis was employed for the synthesis of GaN nanowires
- Post-synthesis decomposition was employed to reduce their diameters to less than 5 nm.

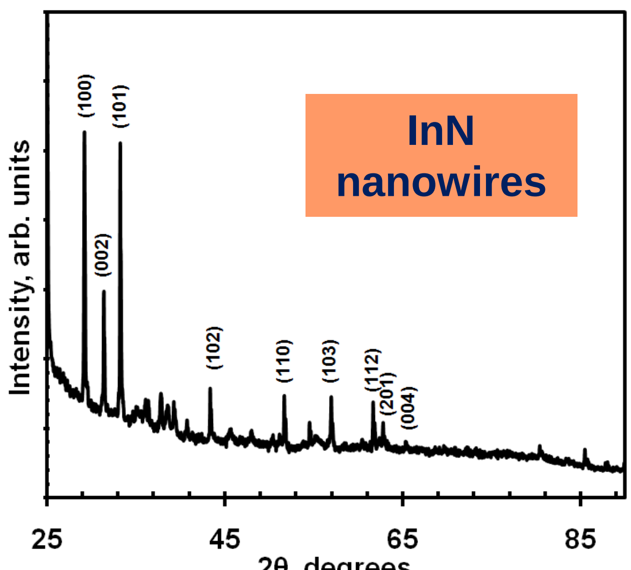
Technical Accomplishment: Synthesis of Zn_3P_2, InN and $CoSb_3$ Nanowires





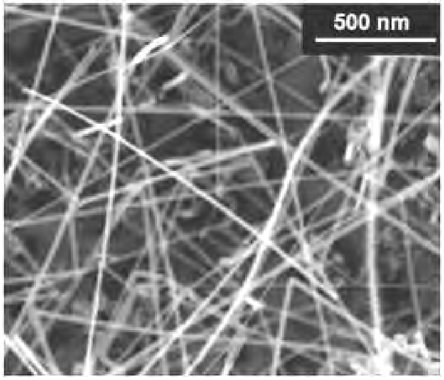




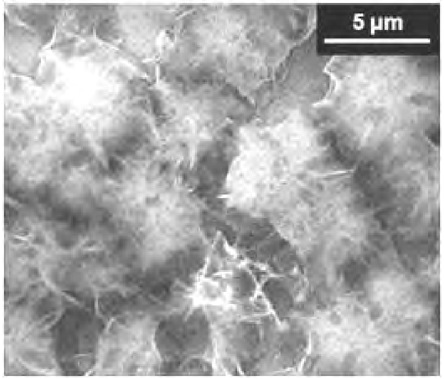


- Self-catalytic synthesis of Zn_3P_2, InN and $CoSb_3$ nanowires has also been accomplished.

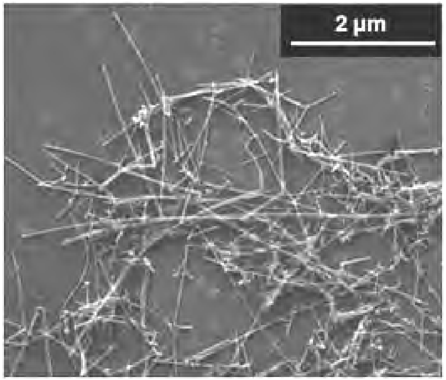
Technical Accomplishment: *In-Situ* Functionalization of Nanowires



As-obtained Zn_3P_2 nanowires



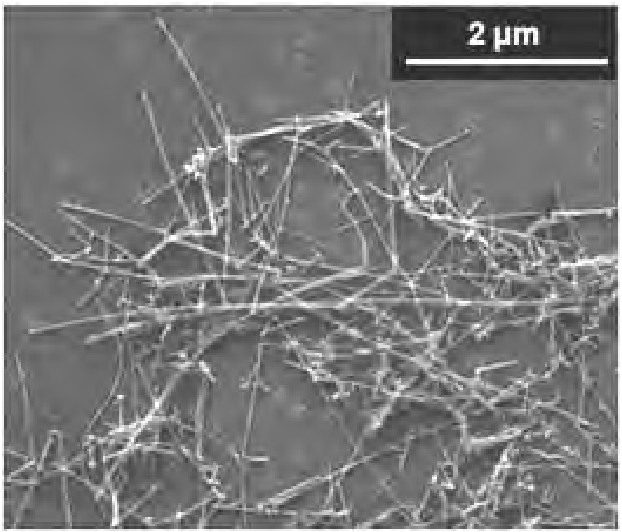
Ex-situ functionalized Zn_3P_2 nanowires



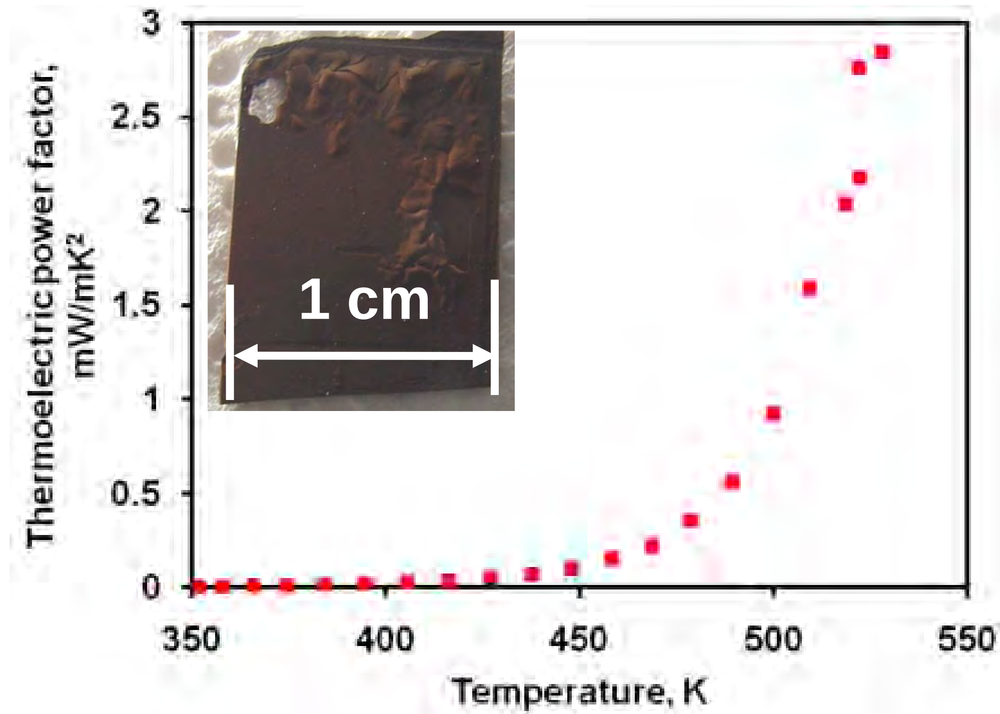
In-Situ functionalized Zn_3P_2 nanowires

- Typically, Zn_3P_2 reacts with moisture and decomposes into $Zn(OH)_2$ and PH_3
- *In-Situ* functionalized Zn_3P_2 nanowires remain stable even after a extended periods of weeks and months, unlike ex-situ functionalized wires.

Technical Accomplishment: Thermopower of Interface-Engineered Nanowire Pellets (Strategy I)



In-situ Functionalized Zn_3P_2 nanowires



- Bulk synthesized nanowire powders were pressed into 1 cm^2 sized pellets the measurement of thermoelectric power factor ($S^2\sigma$).

Future Work: Activities Planned for the Next part of FY 10 and FY 11

- Self-catalytic assisted synthesis of antimonide nanowires, decomposition of nanowires into quantum wires with sub-10 nm diameters.
- Diameter control of the skutterudite quantum wires to 5 nm or less (skutterudite nanowire synthesis has already been accomplished).
- *In-situ* functionalization of the antimonide and skutterudite quantum wires.
- Measurement of the thermoelectric performance of quantum wires assembled using conjugated linker molecules in the temperature range of 25-800 ^{o}C.

Future Work: Activities Planned for FY12

- Systematic study of the effect of linker molecule chemistry on the thermoelectric performance of molecularly wired quantum wire hybrids.
- Microscopic and spectroscopic analysis of the “interface-engineered” inorganic-organic junctions.
- Measurement of the thermoelectric performance of inorganic-organic hybrids comprised of nanowires assembled on top of conducting polymer platforms in the temperature range of 25-800 ^{o}C.
- Finding metals that have low contact resistance with the interface-engineered inorganic-organic hybrids for the fabrication of thermoelectric modules comprised of many thermoelectric cells.

Summary

- This project is aimed at the recovering waste heat from automobile exhaust through the fabrication of inorganic-organic hybrid thermoelectric modules with $zT>3$ performance.
- Inorganic organic hybrid thermoelectric devices will be fabricated using the following components:
  - Inorganic quantum wires with diameters less than 5 nm
  - Conjugated linker molecules (or molecular wires)
  - Functionalized conducting polymer thin films
- Our approach has the following steps:
  - assembling the quantum wires on a large-scale into inorganic-organic hybrid thermoelectric devices by either tethering them to each other or to conducting polymer films through organic molecular linkers, and testing their performance in the 25-800 ^{o}C temperature regime.
  - Assembling thermoelectric devices modules by identifying metals that have low contact resistance with the inorganic-organic hybrids.
- So far, the bulk synthesis and *in-situ* functionalization of Zn_3P_2, InN and $CoSb_3$ nanowire powders has been accomplished.