Inorganic-Organic Hybrid Thermoelectrics

Lance Brockway

for

Sreeram Vaddiraju

Assistant Professor

Department of Chemical Engineering

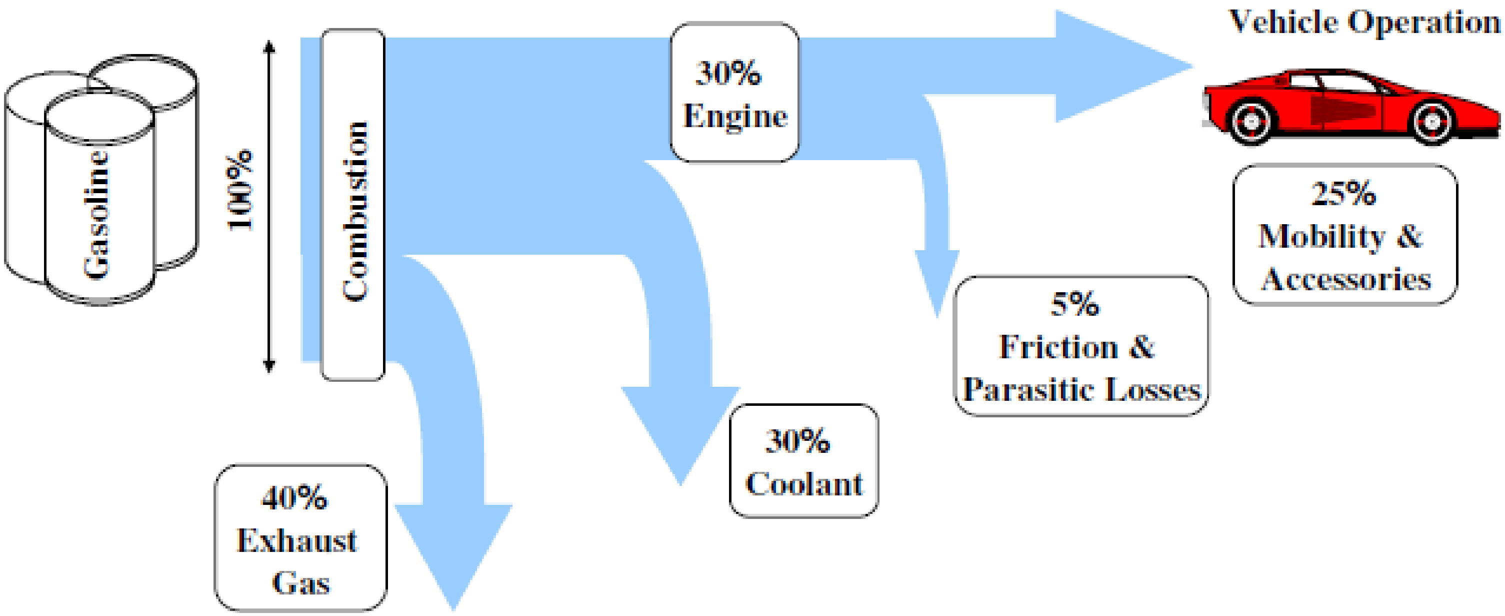
Texas A&M University

Email: Sreeram.vaddiraju@tamu.edu

TEES
TEXAS ENGINEERING EXPERIMENT STATION

TEXAS A&M UNIVERSITY

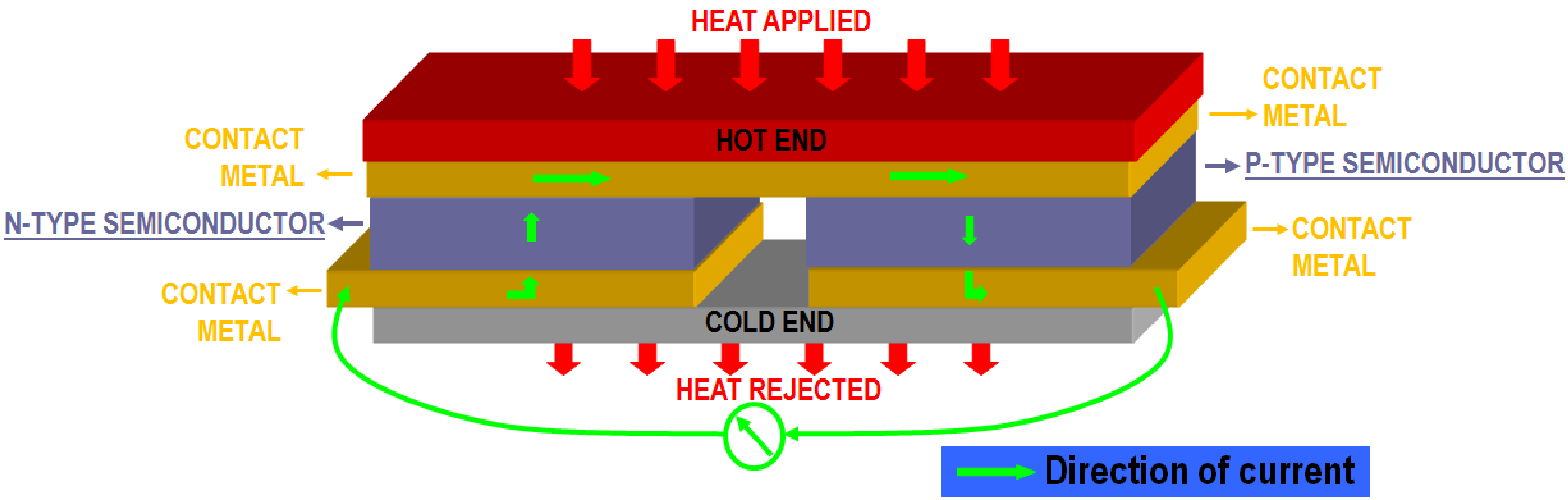
Thermoelectrics for Automobiles



Aim: Fabrication of highly efficient thermoelectric modules for recovering waste heat from automobile exhausts

Yang *et.al*, Journal of Electronic Materials, 38, 1245, 2009.

Principle of Operation of a Thermoelectric Device



Primary Requirements of Thermoelectrics for Automobiles

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

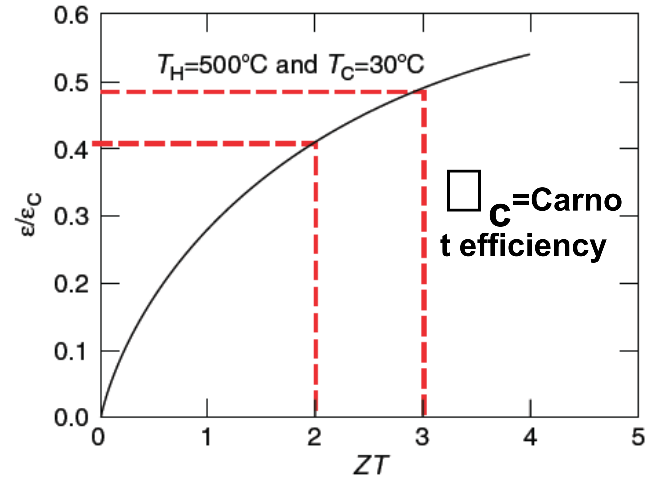
$$ZT = \frac{S^2 \sigma T}{\kappa_e + \kappa_l}$$

<u>Seebeck coefficient</u> (S)

<u>Electrical conductivity</u> (σ)

<u>Electronic thermal conductivity</u> (κ_e)

<u>Lattice thermal conductivity</u> (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 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

Strategy for Enhancing ZT: Tuning the Format of Materials

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

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

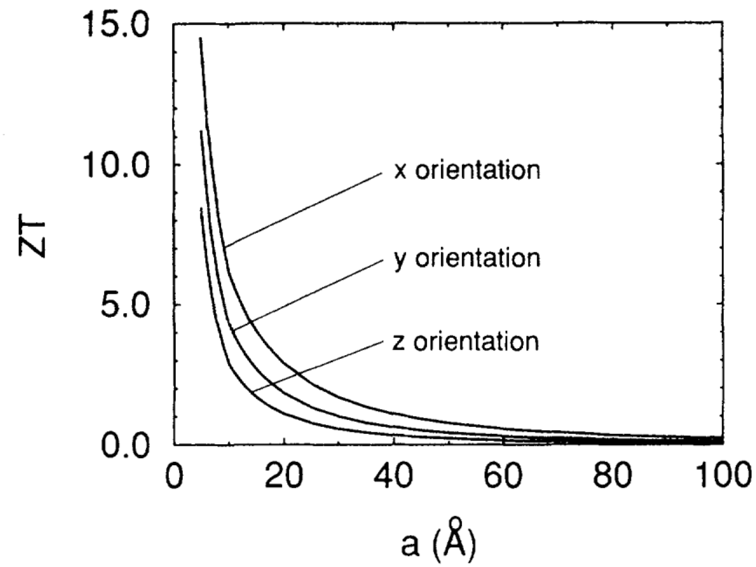
$$\kappa_l = \frac{1}{3}\int c_\lambda(\lambda, T)\, v(\lambda)\, L(\lambda, T)\, d\lambda$$

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 nanomaterials and superlattices with extremely small dimensions, or by a reduction in $L(\lambda, T)$ through enhanced phonon scattering in boundaries and interfaces in nanomaterials and composites.**

Strategy for Enhancing ZT: Tuning the Format of Materials

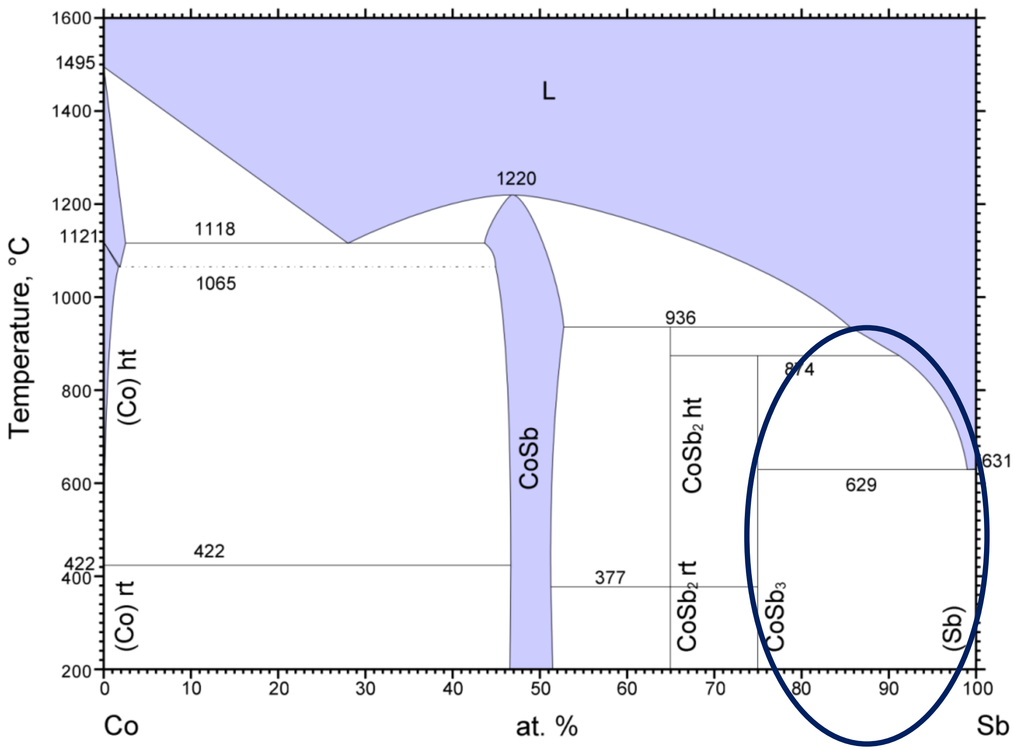
- **Single-crystalline nanowires exhibit good electrical conductivity (*σ*) along their lengths.**
- **Lattice thermal conductivity in nanowires can be scaled to (diameter/roughness)^2, and hence can be reduced through**
  - **a reduction in their diameters (to sub-5 nm length scales)**
  - **enhancing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



- **How can the synthesis of nanowires with sub-5 nm diameters be accomplished in a pristine and contaminant-free 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.

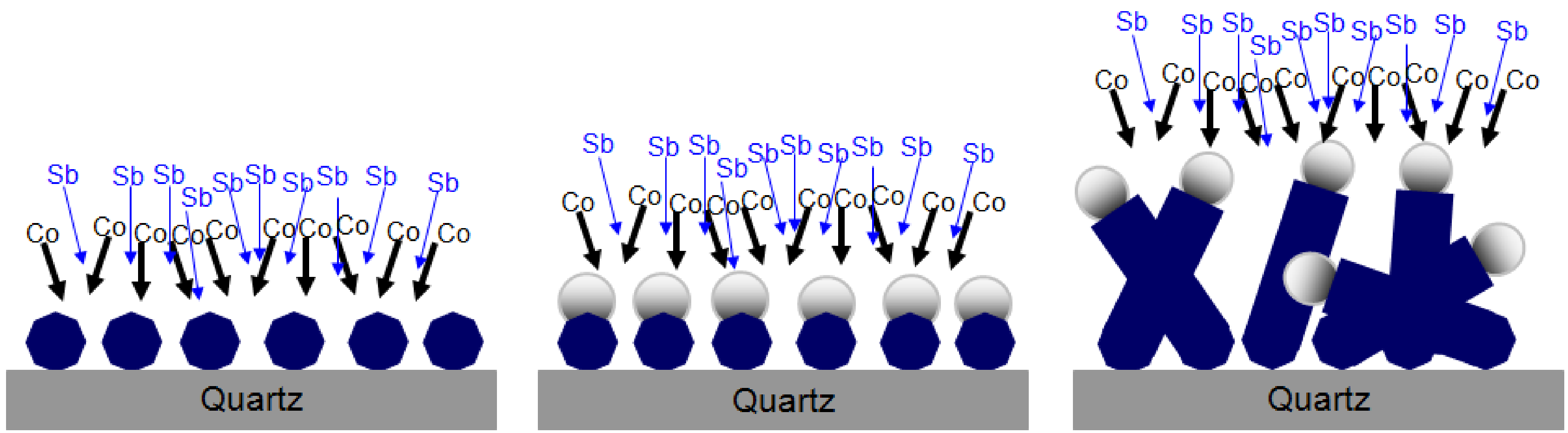
Contaminant-Free Synthesis of Nanowires in a Controlled Manner



- Self-catalysis through antimony (by performing CVD under excess antimony conditions) can be employed for the synthesis of $CoSb_3$ nanowires

•Okamoto , J. Phase Equilib., 12, 244, 1991.

Contaminant-Free Synthesis of Nanowires in a Controlled Manner



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

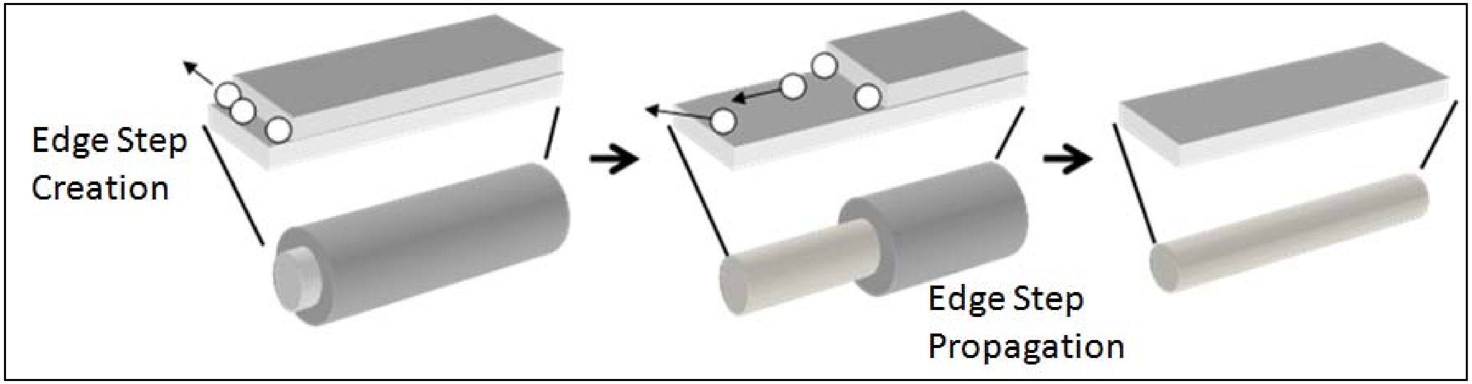
STEP 2: Selective wetting and antimony droplet formation on top of the $CoSb_3$ nuclei

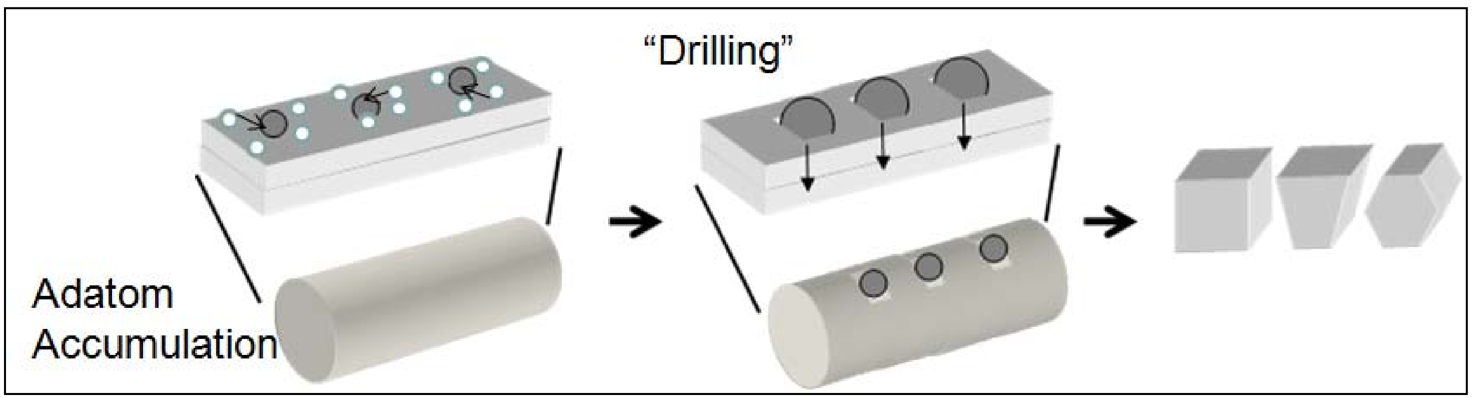
STEP 3: Liquid phase epitaxy through the antimony droplet for $CoSb_3$ nanowire formation

- **Similar procedure yields InSb nanowires**
- **Allows for comparing the effect of nanowire composition ($CoSb_3$ vs. InSb on their *ZT* values**

- **How can the diameters of the obtained nanowires be reduced below 5 nm?**

Post-Synthesis Decomposition for Reducing Diameters of Nanowires



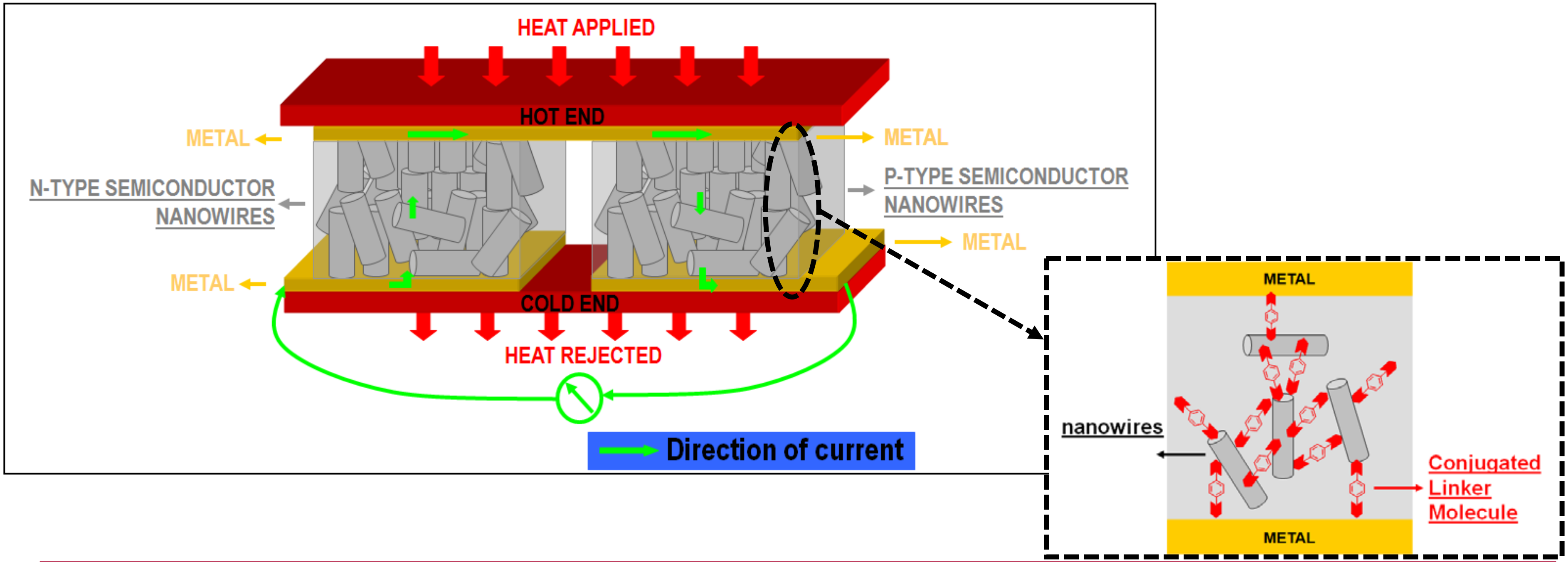


Decomposition at nanoscale, unlike bulk decomposition, occurs in a layer-by-layer fashion.

- **How can large-scale assembly of nanowires, with precisely engineered interfaces, be accomplished?**

Large-scale Assembly of Nanowires

Strategy 1: Molecular wiring of nanowires to each other
- Leads to the formation of nanowire pellets
- Interfacial electrical and thermal transport tunable through variations in the linker molecule chemistry (e.g., 1,3-propanedithiol)

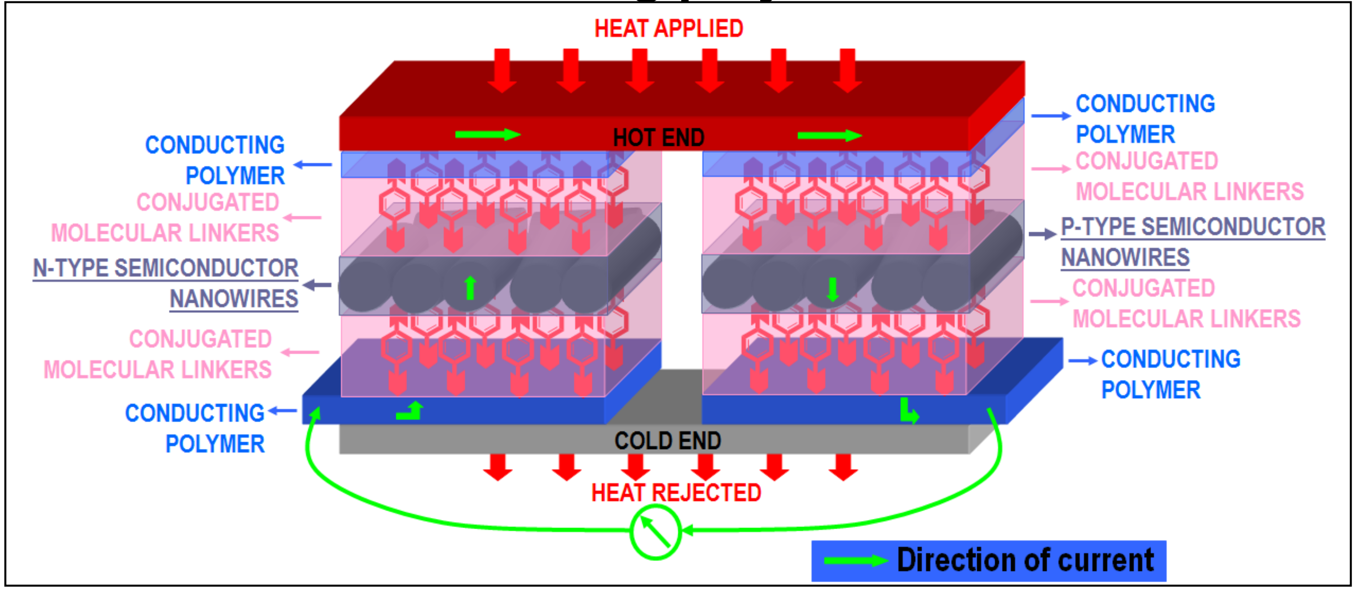


Large-scale Assembly of Nanowires

<u>Strategy 2</u>: Molecular wiring of nanowires to functionalized conducting polymer films

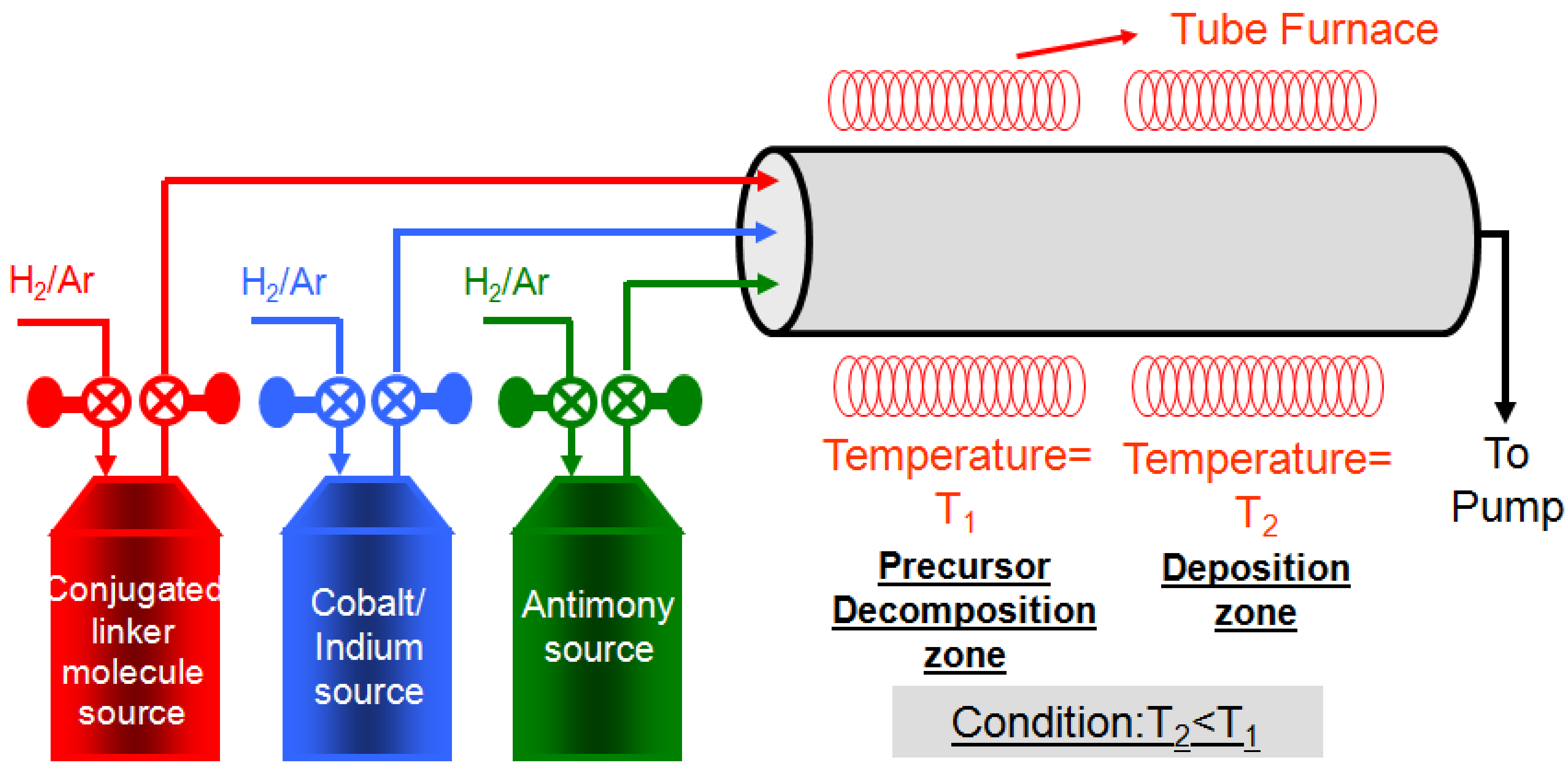
•Uniform assembly of nanowires on functionalized conducting polymer films

•Interfacial electrical and thermal transport tunable through variations in the linker molecule and conducting polymer chemistries



Experimental Setup: Synthesis and *In-situ* Functionalization of Nanowires

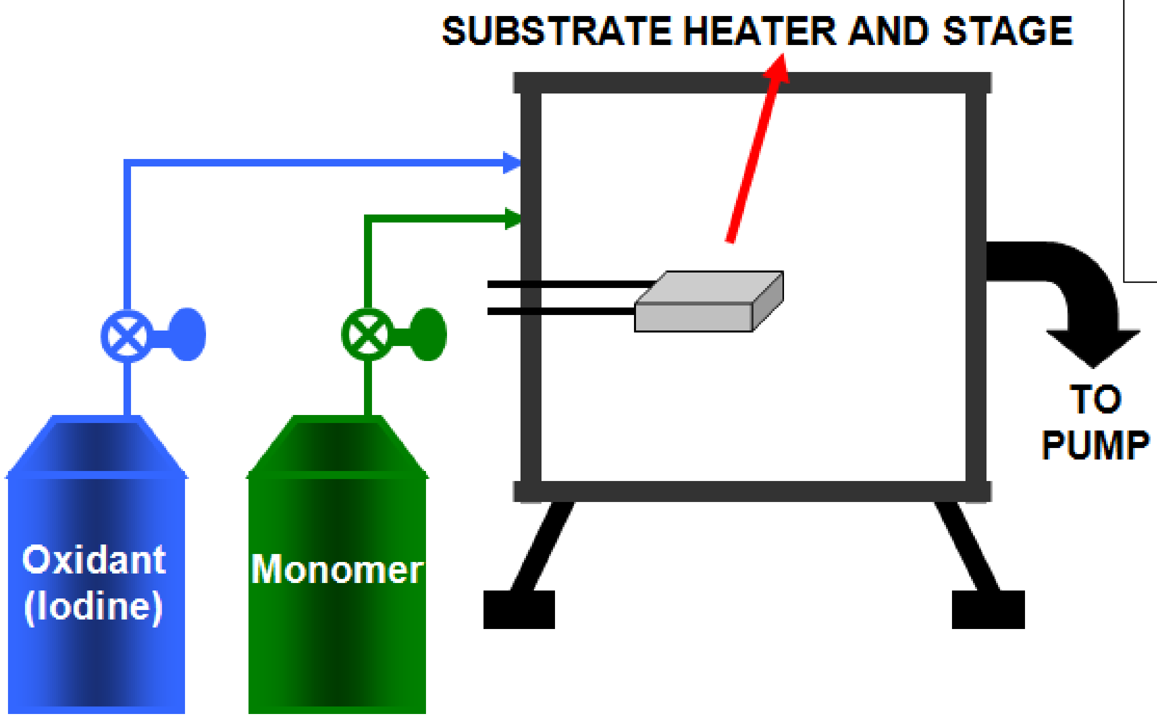
•Self-catalysis, coupled with in-situ functionalization leads to the formation of pristine nanowires, devoid of any oxide shell



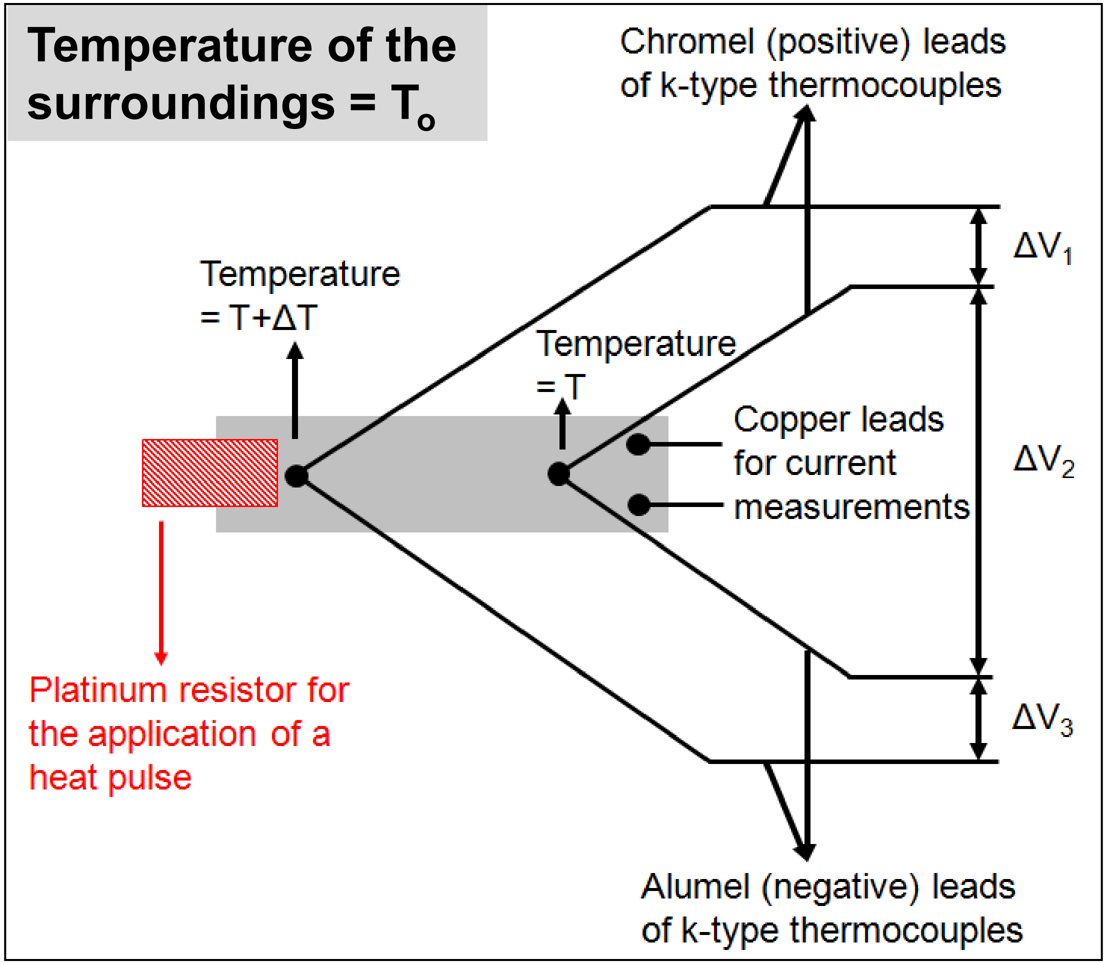
Experimental Setup: Deposition of Conducting Polymers

- Iodine, unlike Fe compounds, is a non-contaminating oxidant
- Iodine is also a more stable dopant

Conducting polymer chemistry



Measurement of S and σ



- **Analogue Subtraction Method**
- **Four-point conductivity measurement**

$$\frac{\Delta V_1}{\Delta V_2} = \frac{(S - S_A)\Delta T}{(S_B - S_A)(T - T_o)}$$

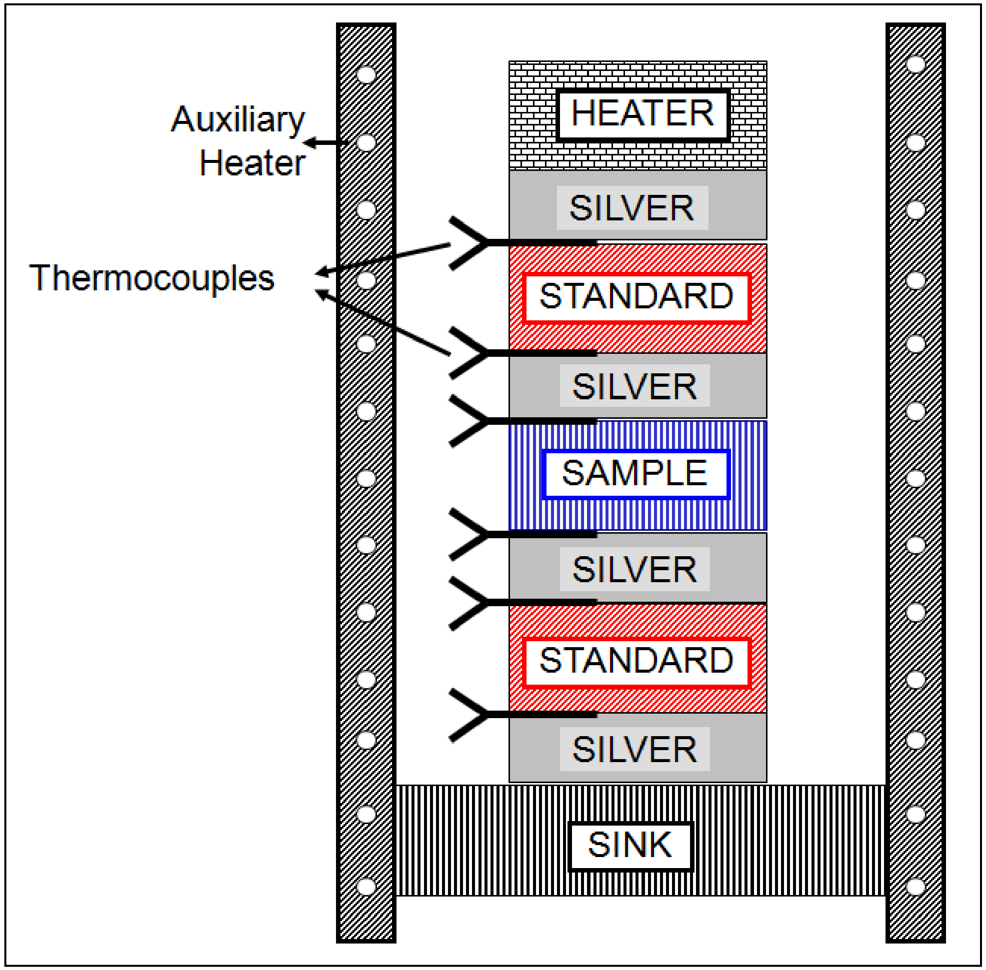
and

$$\frac{\Delta V_3}{\Delta V_2} = \frac{(S - S_B)\Delta T}{(S_B - S_A)(T - T_o)}$$

S_A =Seebeck coefficient of the chromel sides of the thermocouples

S_B= Seebeck coefficient of the alumel sides of the thermocouples

Measurement of κ



- **Comparative method**

$$\kappa = \frac{(\kappa_{ST})\left(\Delta T / \Delta X\right)_{ST}}{\left(\Delta T / \Delta X\right)}$$

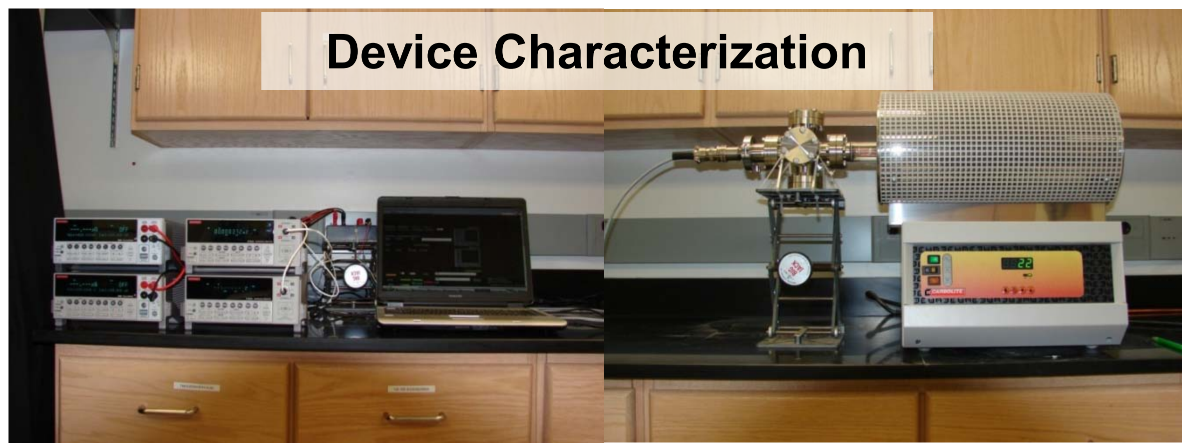
κ_{ST} is the thermal conductivity of the standard

$(\Delta T / \Delta X)$ is the temperature gradient

Equipment


CVD chamber for material synthesis

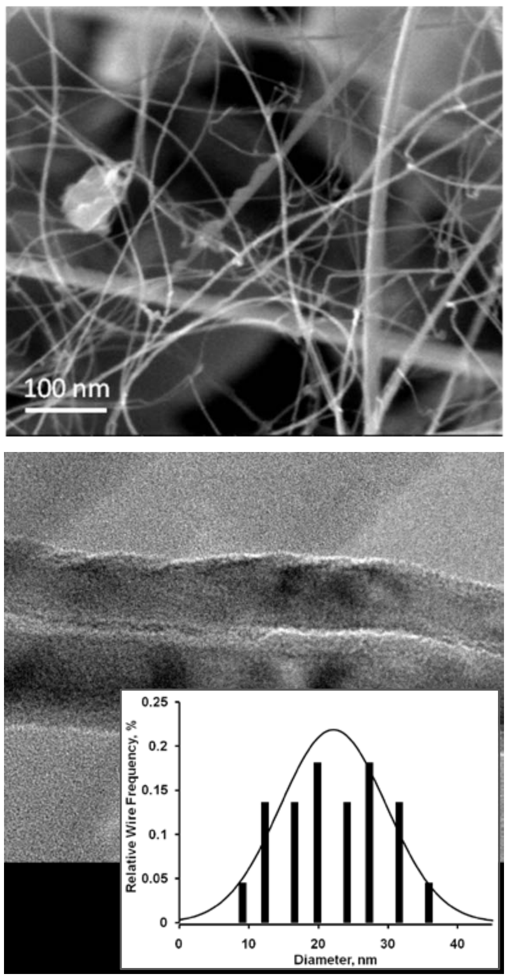

Material synthesis


Device Characterization

TEES TEXAS ENGINEERING EXPERIMENT STATION

TEXAS A&M UNIVERSITY

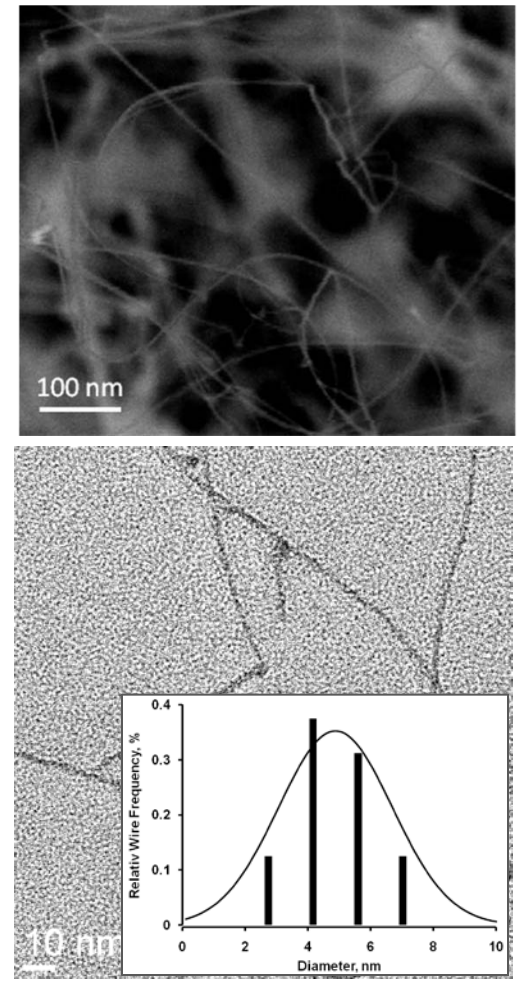
Preliminary Results: GaN Nanowire and Quantum Wire Synthesis



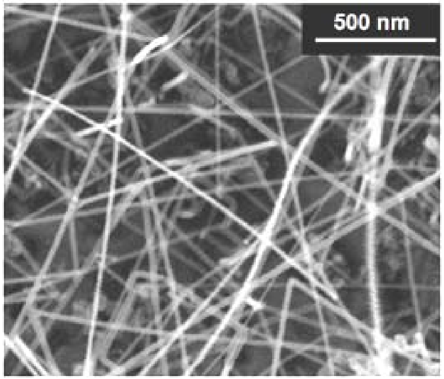
900 C

$\longrightarrow$

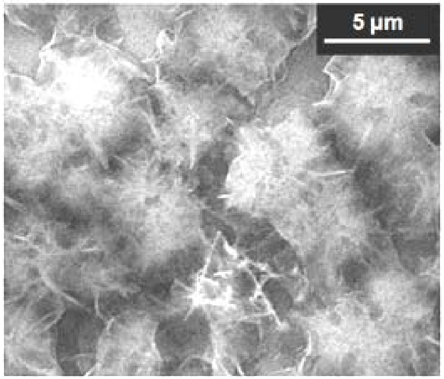
NH_3



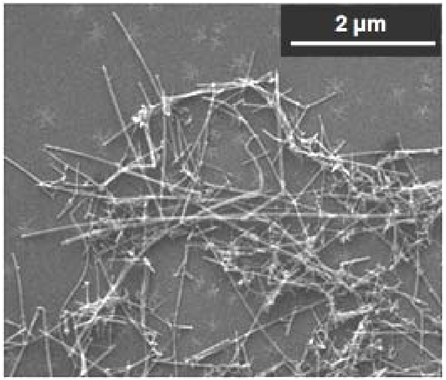
Preliminary Results: Zn_3P_2 Nanowire Synthesis and In-Situ Functionalization



As-obtained Zn_3P_2 nanowires



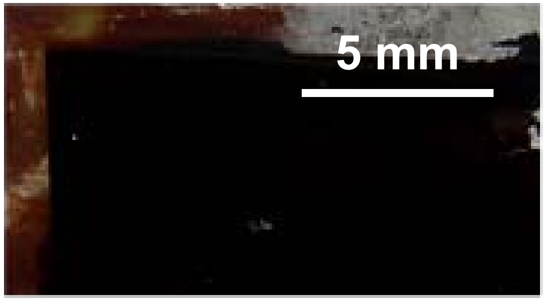
Ex-situ functionalized Zn_3P_2 nanowires



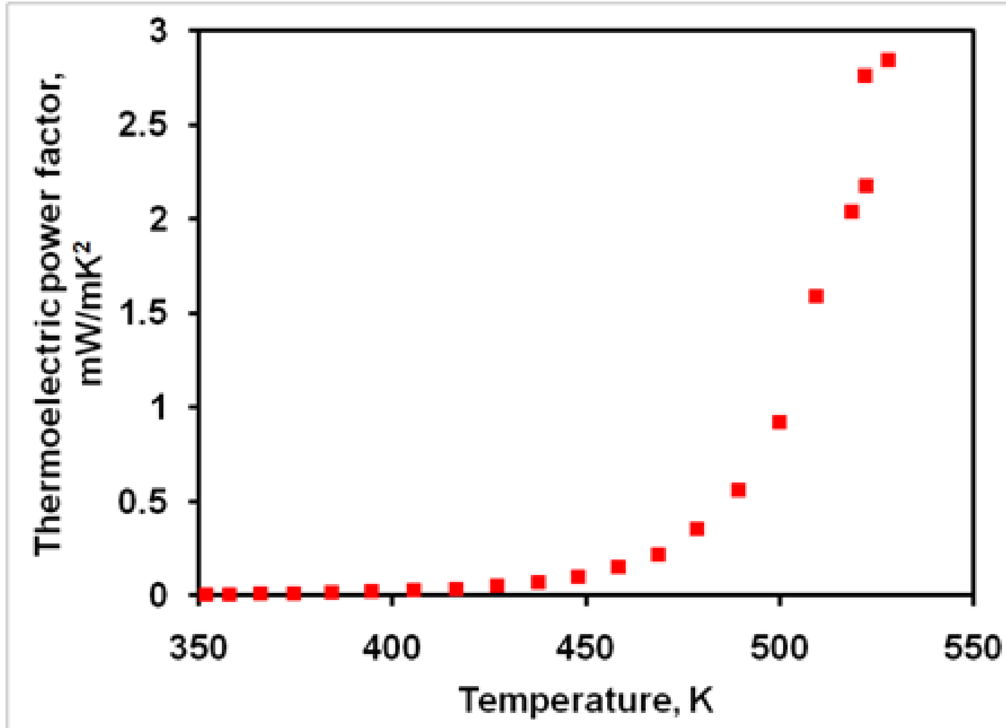
In-Situ functionalized Zn_3P_2 nanowires

- 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

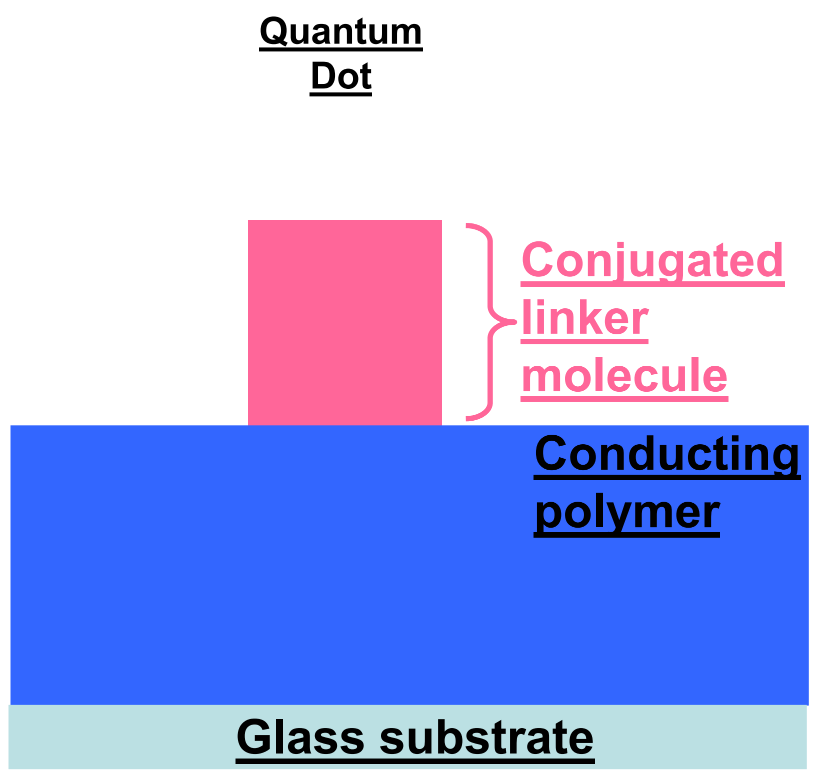
Preliminary Results: Thermoelectric power factor of 4-aminothiophenol Functionalized Zn_3P_2 Nanowire Mats

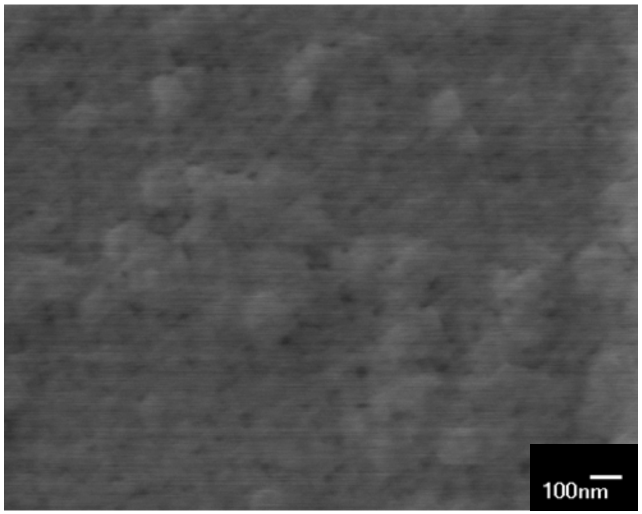


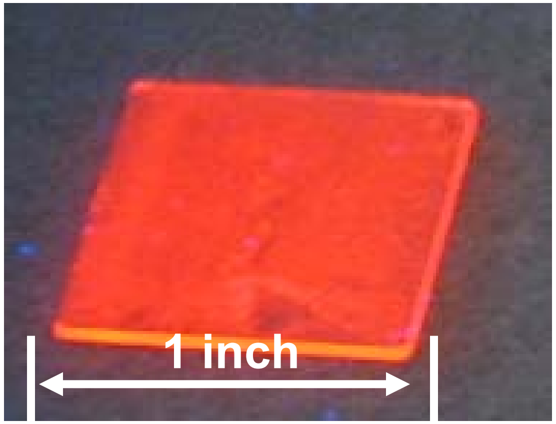
The thermoelectric power factor ($s^2\sigma$) of 4-aminothiophenol functionalized Zn_3P_2 nanowire pellets increases with temperature



Preliminary Results: Large-Scale Assembly of Inorganic Nanomaterials on Conducting Polymers







Chemical Engineering at Texas A&M University - Mozilla Firefox

File Edit View History Bookmarks Tools Help

http://www.che.tamu.edu/people/faculty/info?fid=103

Most Visited Getting Started Latest Headlines EERE Financial Opport...

Chemical Engineering at Texas A&M ...

Home News Che Intranet Give Now Search Contact Us Students Our Department Assessment

Artie McFerrin Department of
CHEMICAL ENGINEERING | TEXAS A&M ENGINEERING

TAMU / Engineering / Chemical Engineering / People / Faculty / Sreeram Vaddiraju

Sreeram Vaddiraju

Assistant Professor

Telephone: (979) 862-1615
Fax Number: (979) 845-6446
E-mail: Sreeram.Vaddiraju@chemail.tamu.edu

Mailing Address...
237 Jack E. Brown Engineering Building
3122 TAMU
College Station, TX 77843-3122

Education

Ph.D., University of Louisville, 2006
M.S., University of Louisiana, 2002
B. Tech., Andhra University, India, 2000

Research Interests

Dr. Vaddiraju' research work focuses on the development of novel vapor phase techniques for the synthesis of organic and inorganic nanostructures and the development and implementation of novel in-situ and ex-situ schemes for the large-scale integration of these nanostructures into energy conversion devices (e.g., solar cells, thermoelectric devices).

Selected Publications

S. Vaddiraju, K. Senecal, Karen K. Gleason, 'Novel strategies for the deposition of -COOH conducting copolymer films and assembling inorganic nanoparticles on conducting polymer platforms', Advanced Functional Materials, 18, 1929, 2008.

Research Plan

Task	Timeline (Months)					
	0-6	6-12	13-18	19-24	25-30	31-36
Self-catalysis synthesis of skutterudite and antimonide nanowires, decomposition of nanowires into quantum wires with sub-10 nm diameters						
Measurement of the thermoelectric performance of individual wires and wires assembled using conjugated linker molecules						
Measurement of the thermoelectric performance of inorganic-organic hybrids comprised of nanowires assembled on top of conducting polymer platforms						
Microscopic and spectroscopic analysis of the “interface-engineered” inorganic-organic and inorganic-inorganic junctions						
Determination of the contact resistances of metal-hybrid junctions using transfer length method for various metals in contact with the proposed hybrids						
Determination of thermoelectric performance of devices with areas greater than 1 inch^2						

Additional Information: Why $CoSb_3$ and InSb?

- InSb has a zincblende crystal structure with very large Bohr exciton radius of 54 nm and high mobility of 7.8×10^4 $cm^2V^{-1}S^{-1}$. The large Bohr exciton radius of InSb makes it an ideal candidate for understanding its thermoelectric behavior under quantum confined conditions.
- $CoSb_3$ has a skutterudite structure with empty cages in the lattice. Phonon scattering could also be enhanced and hence the lattice thermal conductivity could be reduced in skutterudites by either employing quantum wires with diameters less than the mean free path of the phonons or by filling the cages with foreign atoms.

TEXAS ENGINEERING EXPERIMENT STATION

TEXAS A&M UNIVERSITY