

CNT-based Thermal Interface Materials for Load-Bearing Aerospace Applications

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Objective

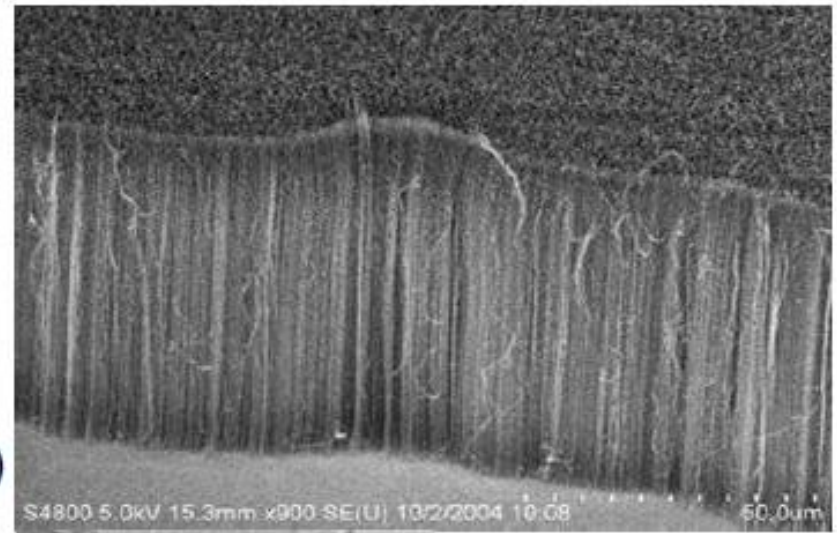
Develop multifunctional CNT-epoxy Thermal Interface Materials (TIMs) for load bearing aerospace applications.

Emphasis -

To increase thermal transport across a thermal interface by utilizing an array of Vertically Aligned MWCNTs.

Target k – 5 -7 W/(m-K)

SEM picture of an array of vertically aligned carbon nanotube array grown on a silicon substrate.

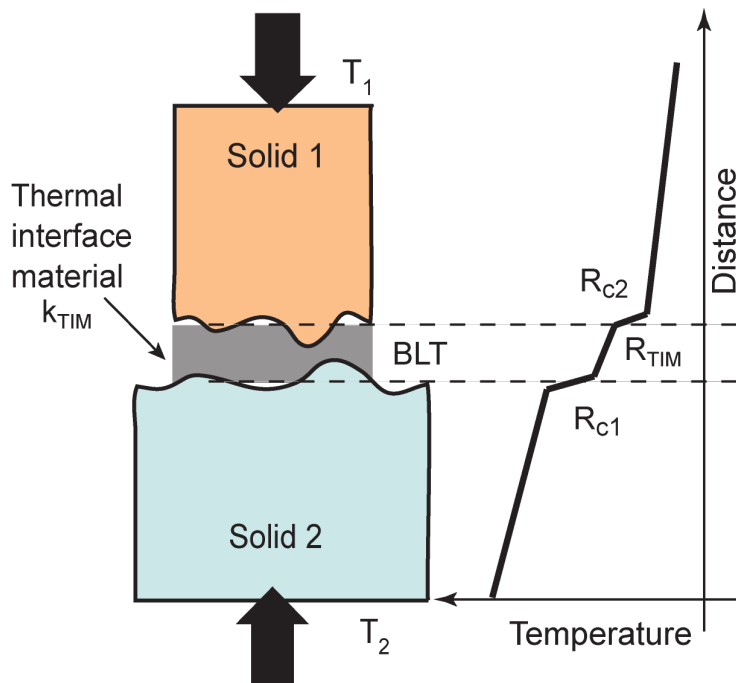


Typical Thermal Interface

Total Thermal Interfacial Resistance

$$R_{\text{interface}} = R_{c1} + \frac{BLT}{k_{\text{TIM}}} + R_{c2}$$

BLT – boundary layer thickness



Minimize $R_{\text{interface}}$

$k_{\text{TIM}} \uparrow$

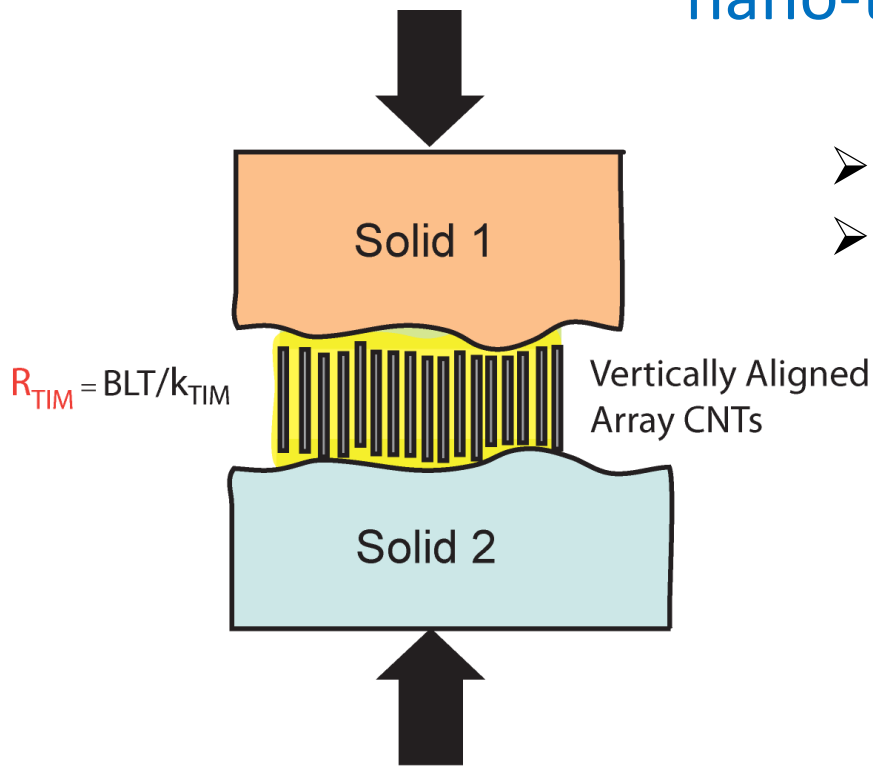
- Use high thermal conductivity fillers
- Minimize number of thermal interfaces

$R_c \downarrow$

- Reduce air gaps – use smooth contacting surfaces
- employ low melt-point materials (e.g. Sn), as capping layers
- materials with compatible phonon spectra

Approach

Vertically-aligned multi-wall Carbon nano-tubes in an epoxy matrix



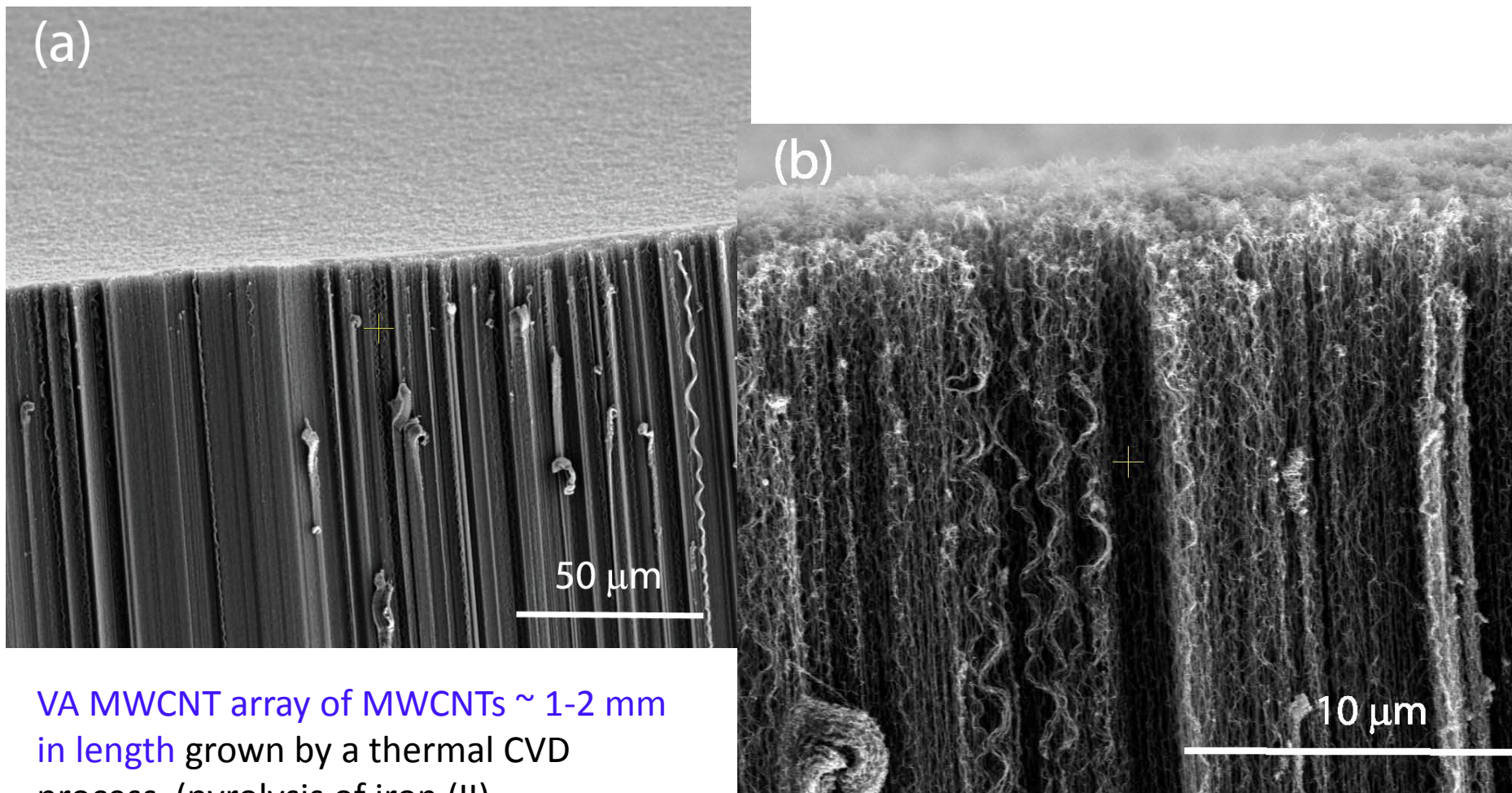
- $k_{CNT} \sim 100$ W/m-K
- Use Sn capping metal layer to minimize phonon scattering at CNT-epoxy ends.

Assume 10% vol. fraction of VACNT in an epoxy matrix

($k_{epoxy} \sim 0.25$ W/m-K; $k_{CNT} \sim 100$ W/m-K)

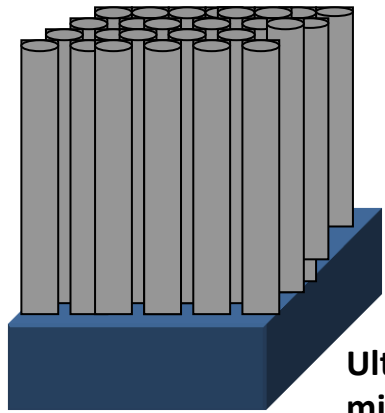
$k_{TIM} \sim 10$ W/m-K

VA Multi-walled CNT Array

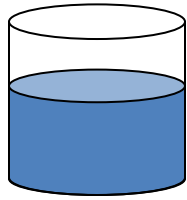


VA MWCNT array of MWCNTs ~ 1-2 mm in length grown by a thermal CVD process (pyrolysis of iron (II) phthalocyanine (FePc) under Ar/H₂ at 900 °C on a silicon wafer). Nanotube dia. 15 to 40nm.

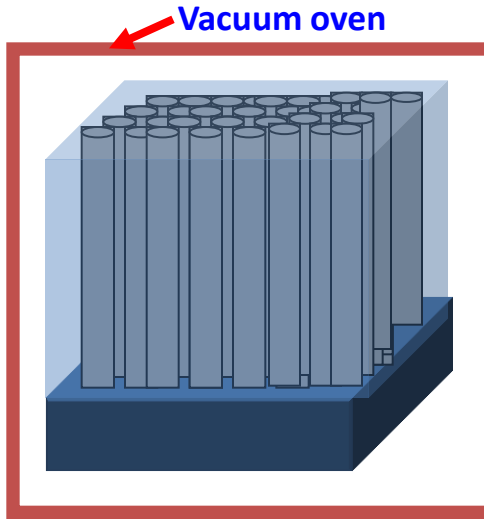
Fabrication of VACNT- epoxy Composite TIM



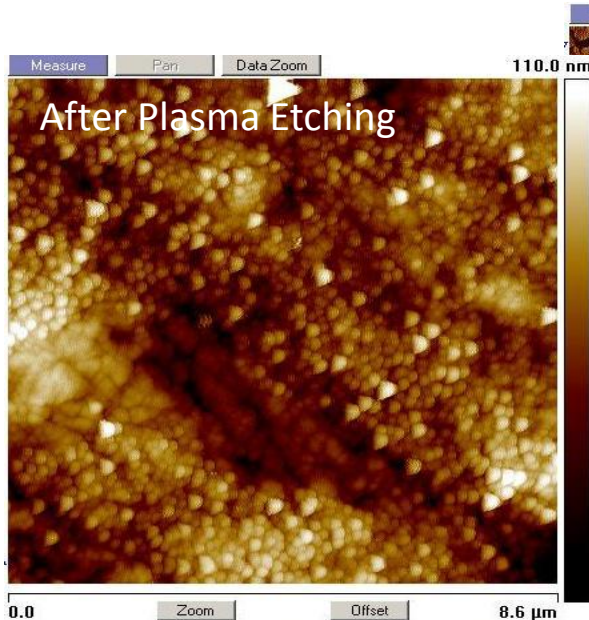
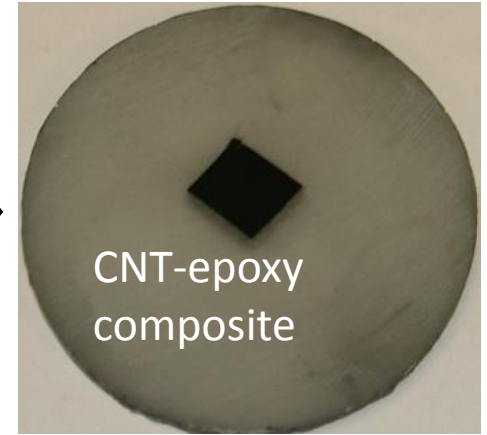
VA MWCNT Array on Si



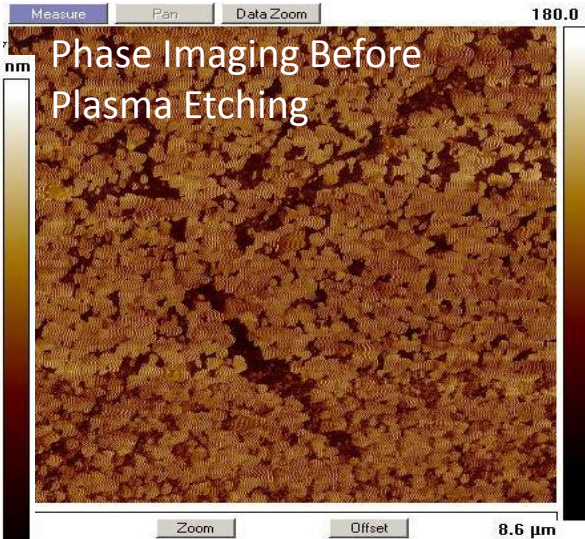
Ultrasonicated mixture of Epoxy resin + curing agent + solvent Epon 862



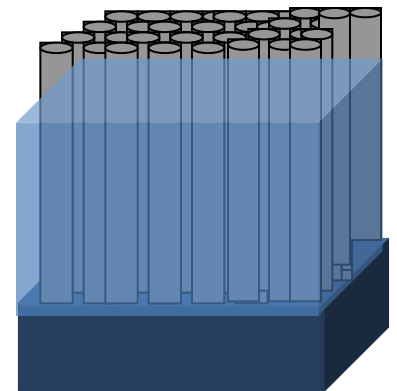
VA MWCNT Array -- spin coat with epoxy, and cured



After Plasma Etching

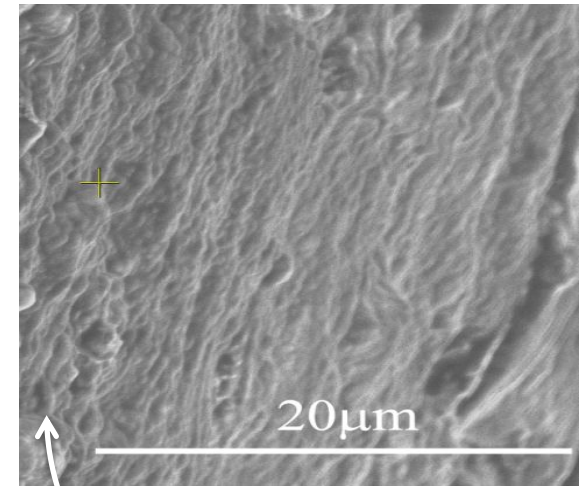
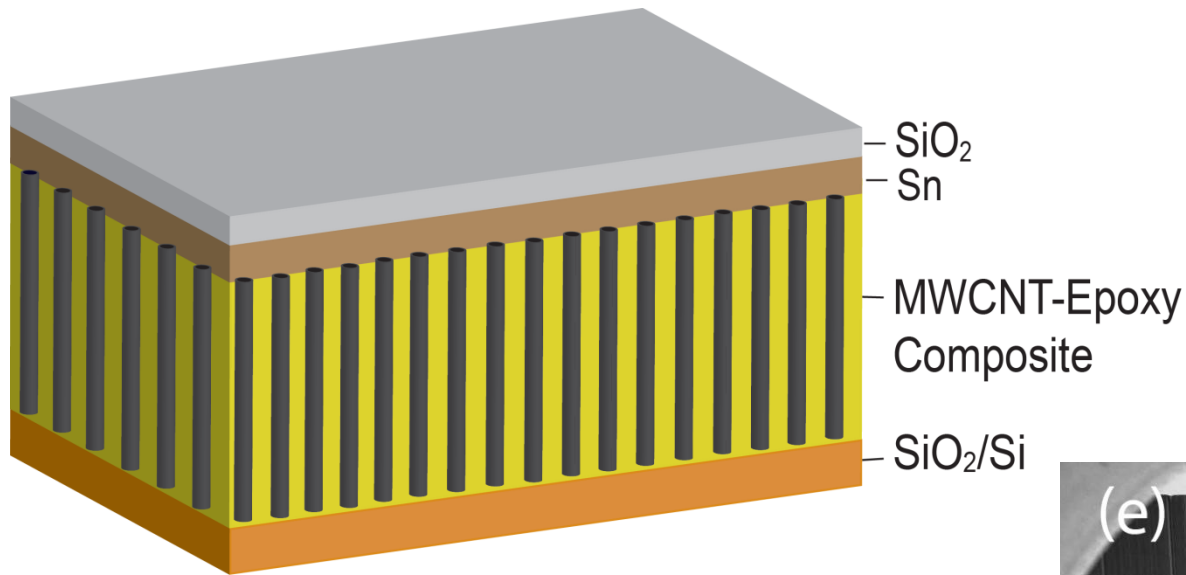


Phase Imaging Before Plasma Etching



Oxygen Plasma Etch to expose CNT tips

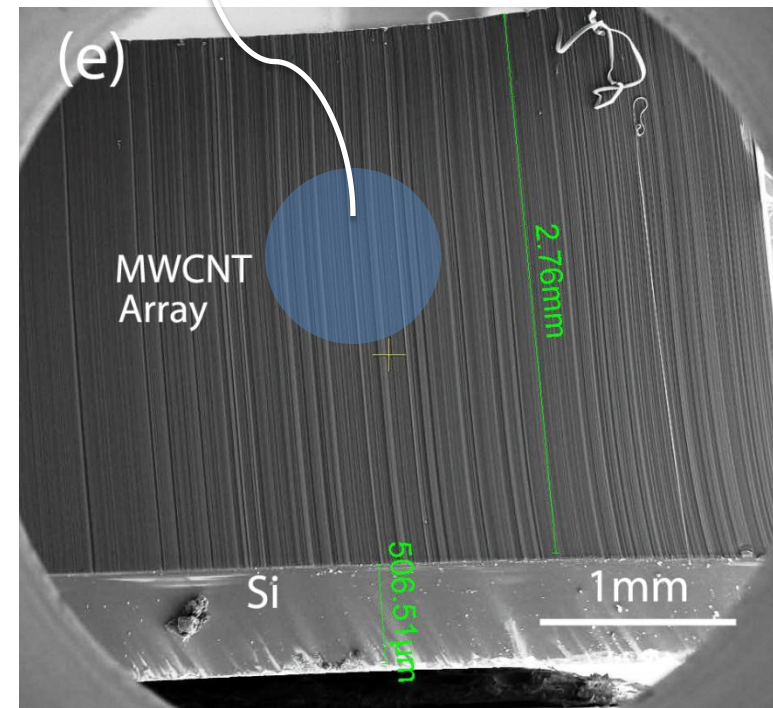
Vertically Aligned MWCNT-epoxy Composite



Tasks: Characterize Thermal Transport across MWCNT-epoxy TIM

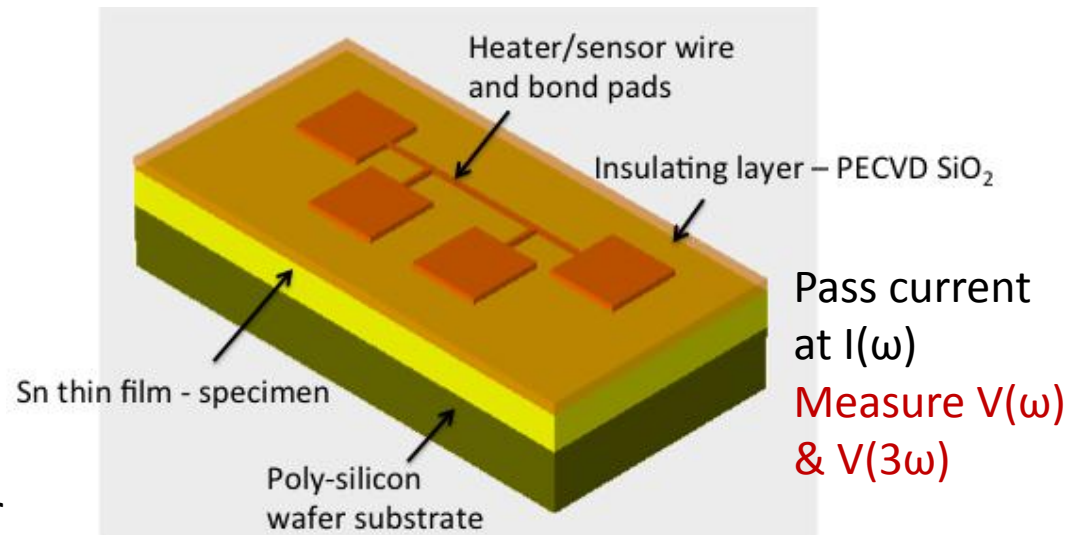
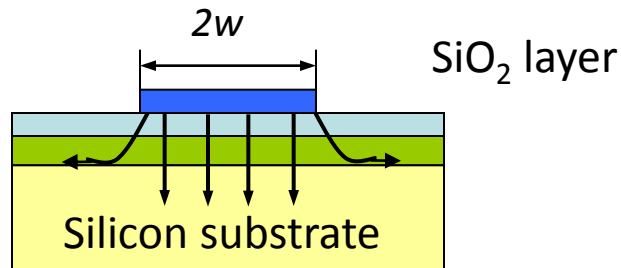
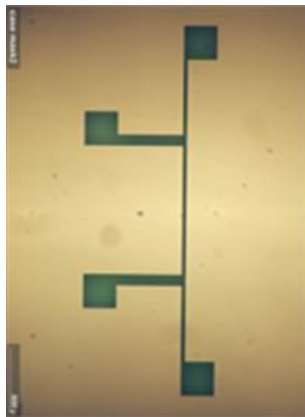
Individual components

- Individual MWCNTs; epoxy matrix;
- Sn capping layer
- Interfacial thermal resistance at the MWCNT ends & capping Layer



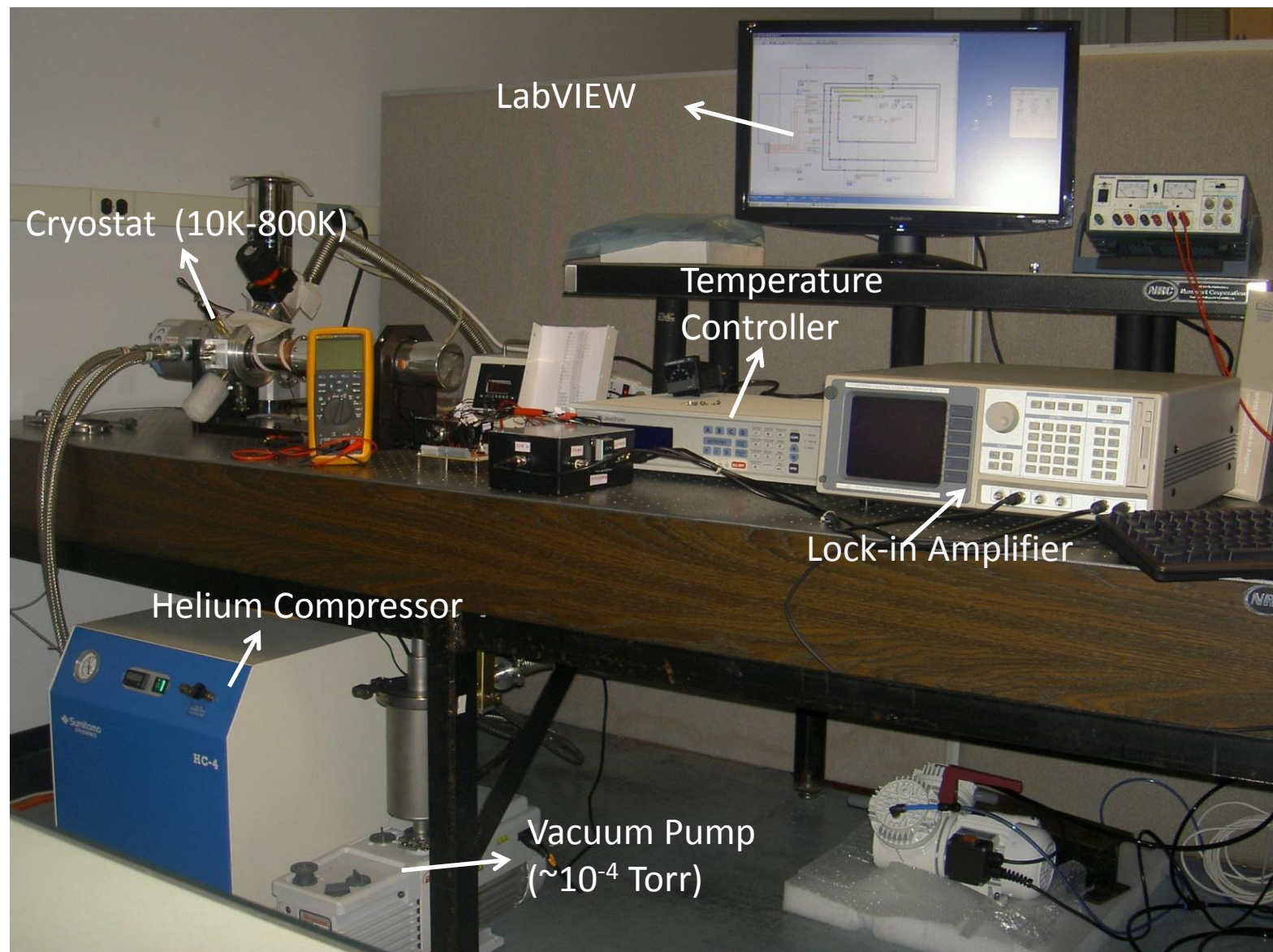
Thermal conductivity of Tin (Sn) Capping layer -- 3 Ω Technique

- 99.999 % pure Sn (100 nm & 500 nm) sputtered on Si substrate at 2×10^{-7} Torr
- Insulating film – SiO₂ (PECVD using TEOS precursor at 150°C)
- Heater Lines – deposit Al using magnetron sputtering along with a microfabricated shadow mask

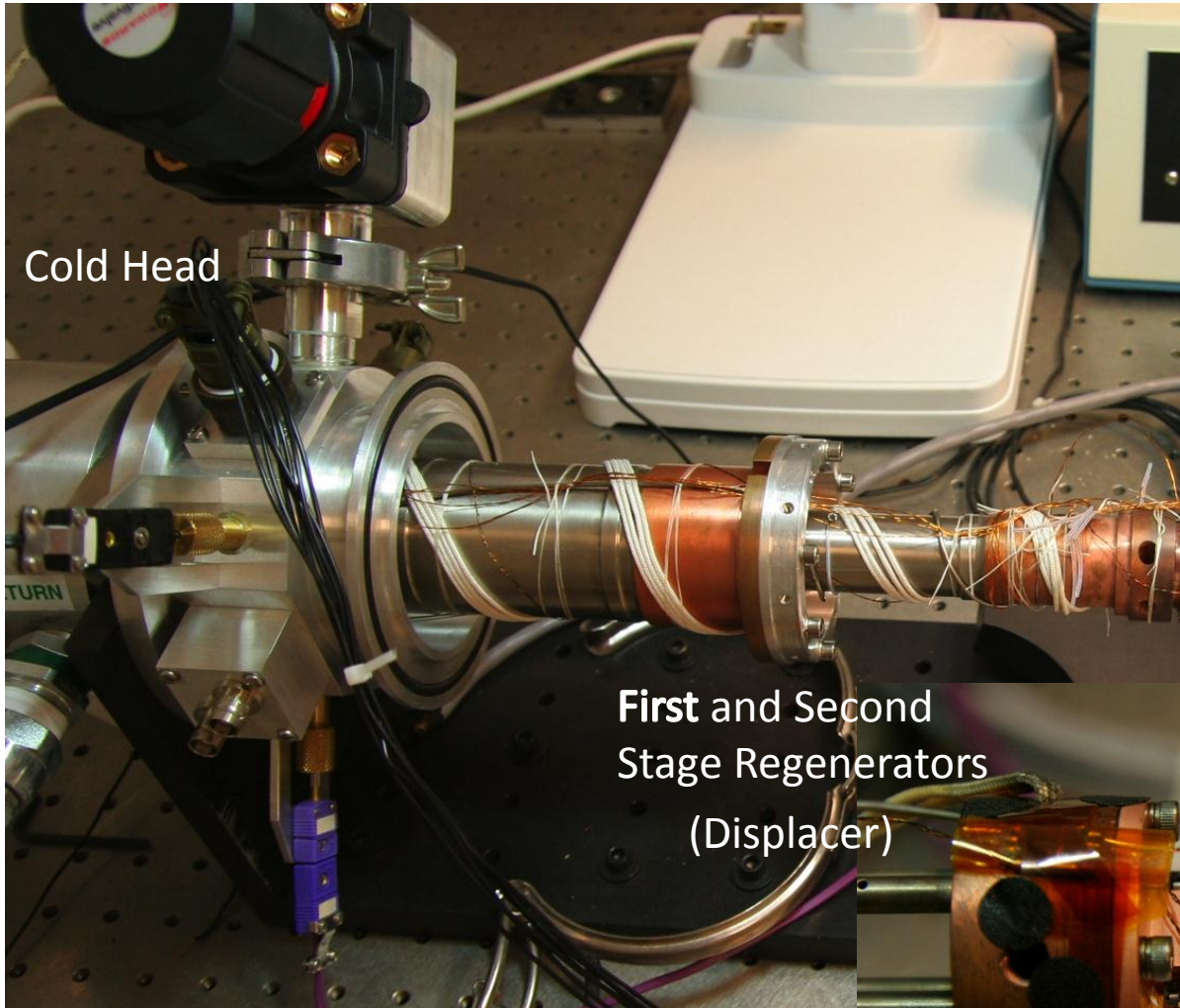


Thin Film Cross-Plane Thermal Conductivity

3 Ω Experimental Setup



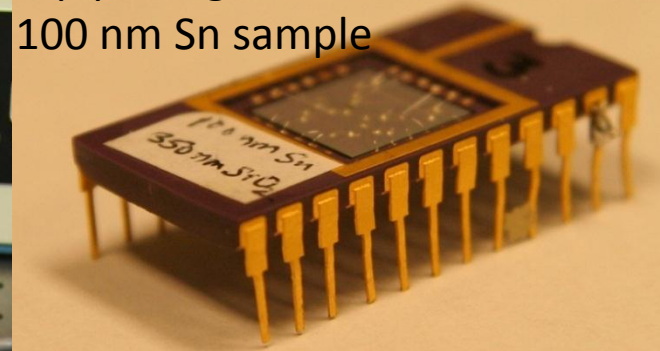
Cryostat with Specimen



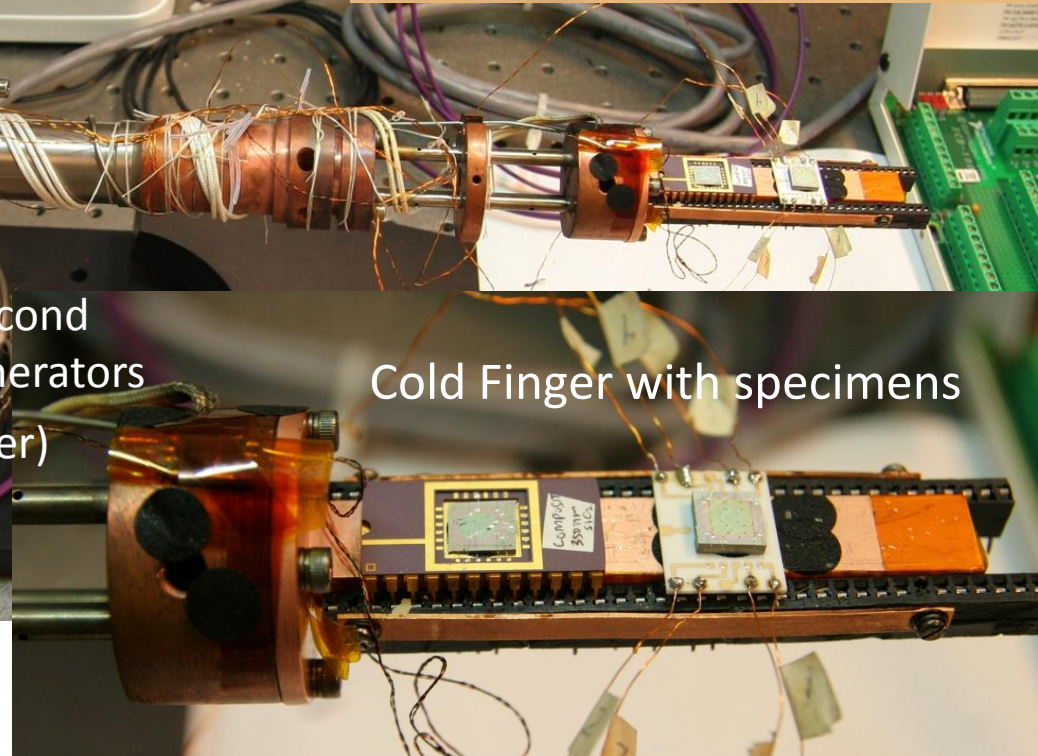
Cold Head

First and Second
Stage Regenerators
(Displacer)

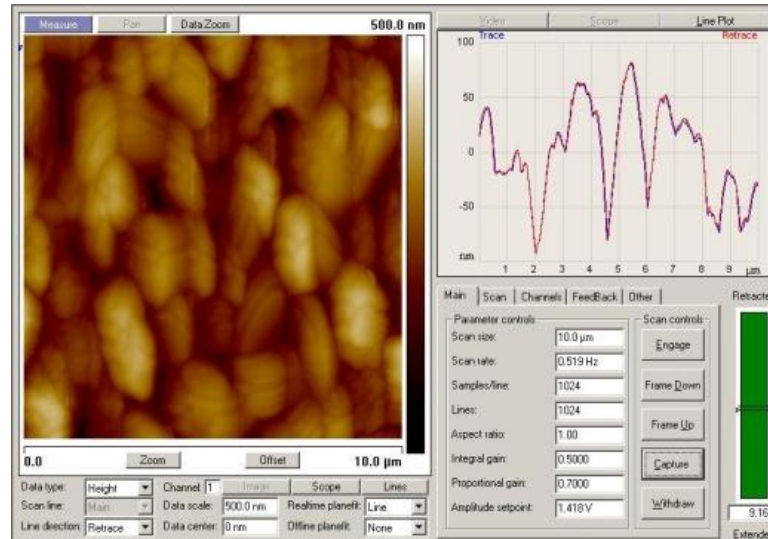
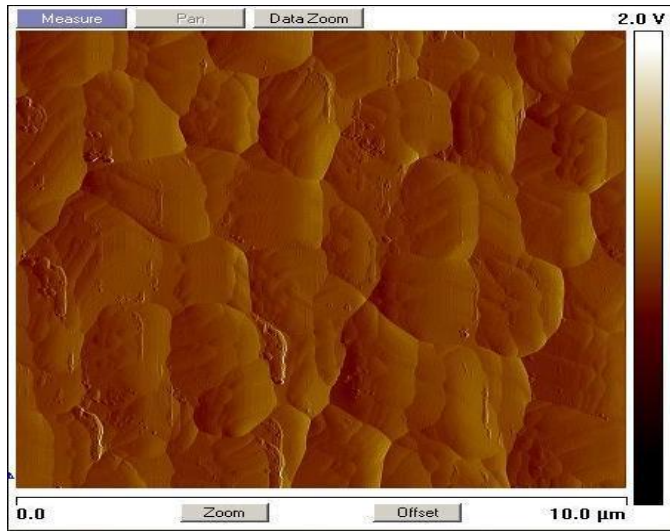
Dip package with
100 nm Sn sample



Cold Finger with specimens

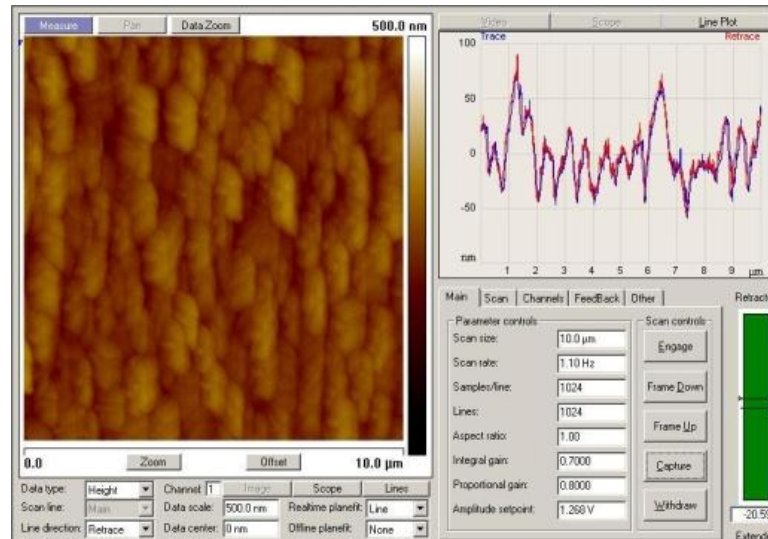
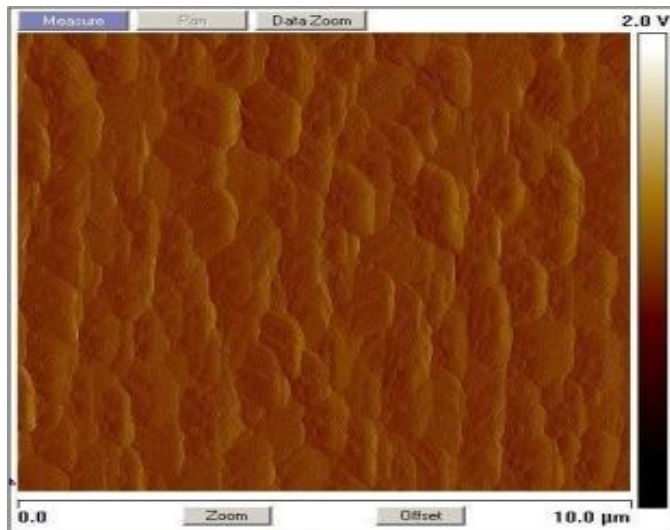


Sn Thin Film specimens (500 & 100 nm thick)



500 nm Sn film

Grain size:
450 to 2000 nm

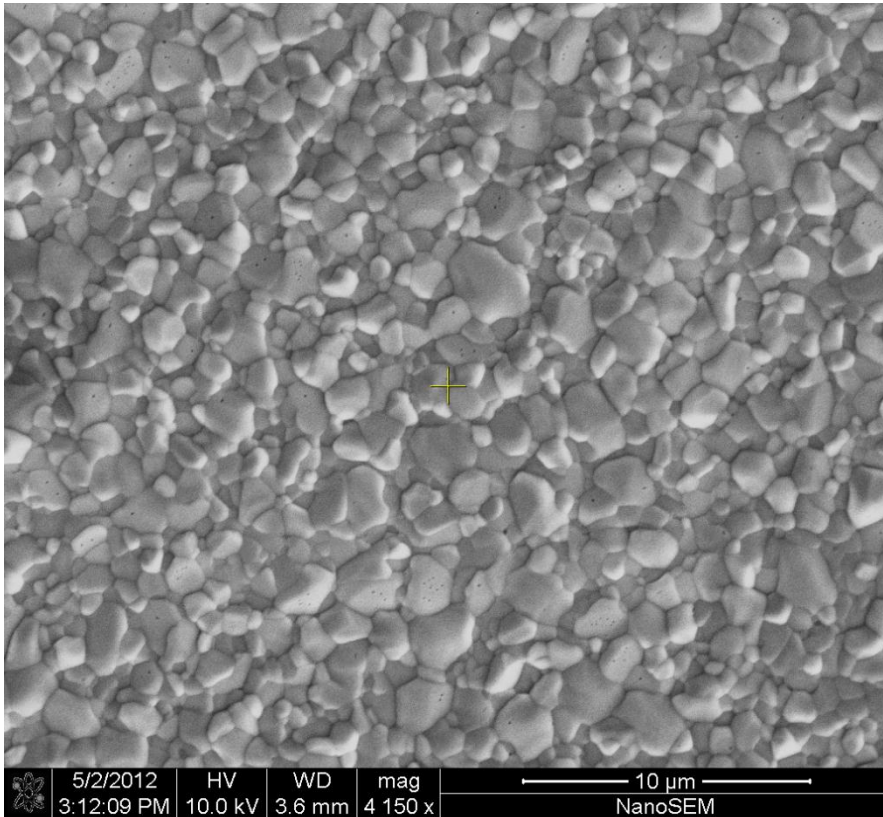


100 nm Sn film

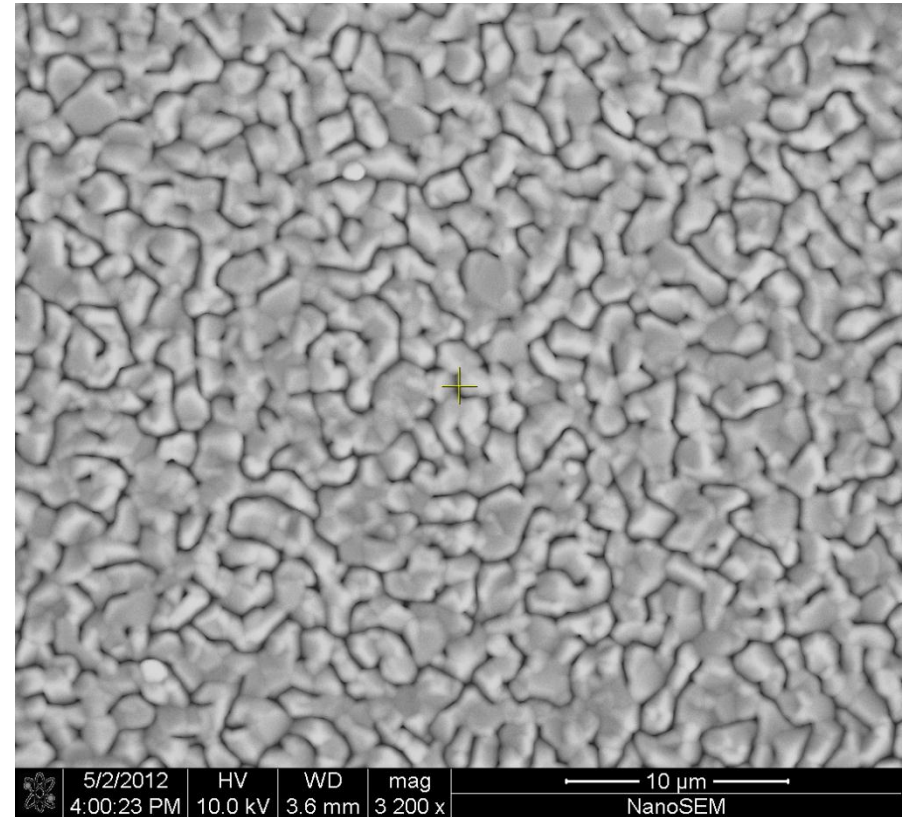
Grain size:
150 to 600 nm

Twin boundaries
within grains

SEM Micrographs



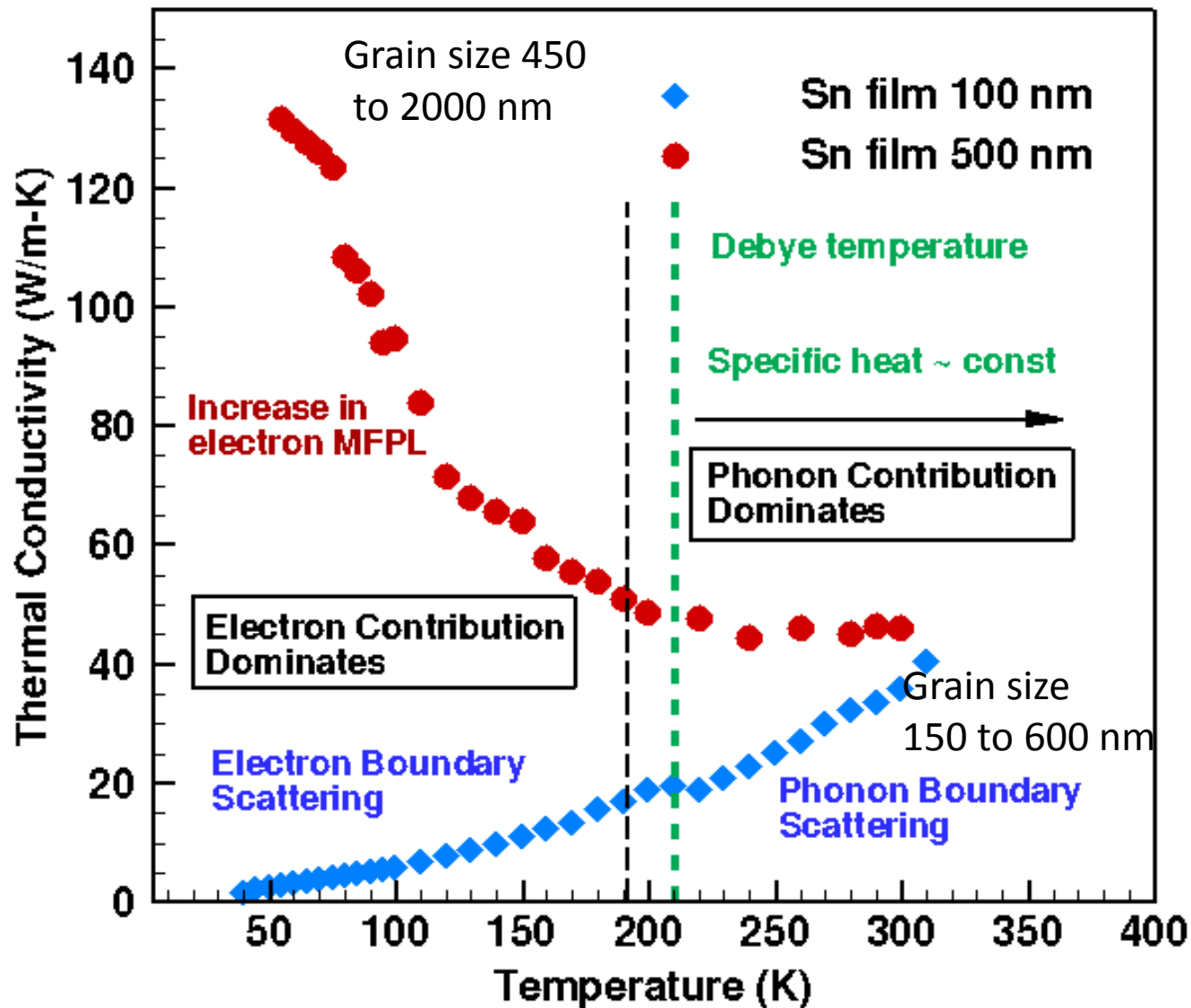
500 nm thickness



100 nm thickness

Thermal conductivity of Sn thin Films

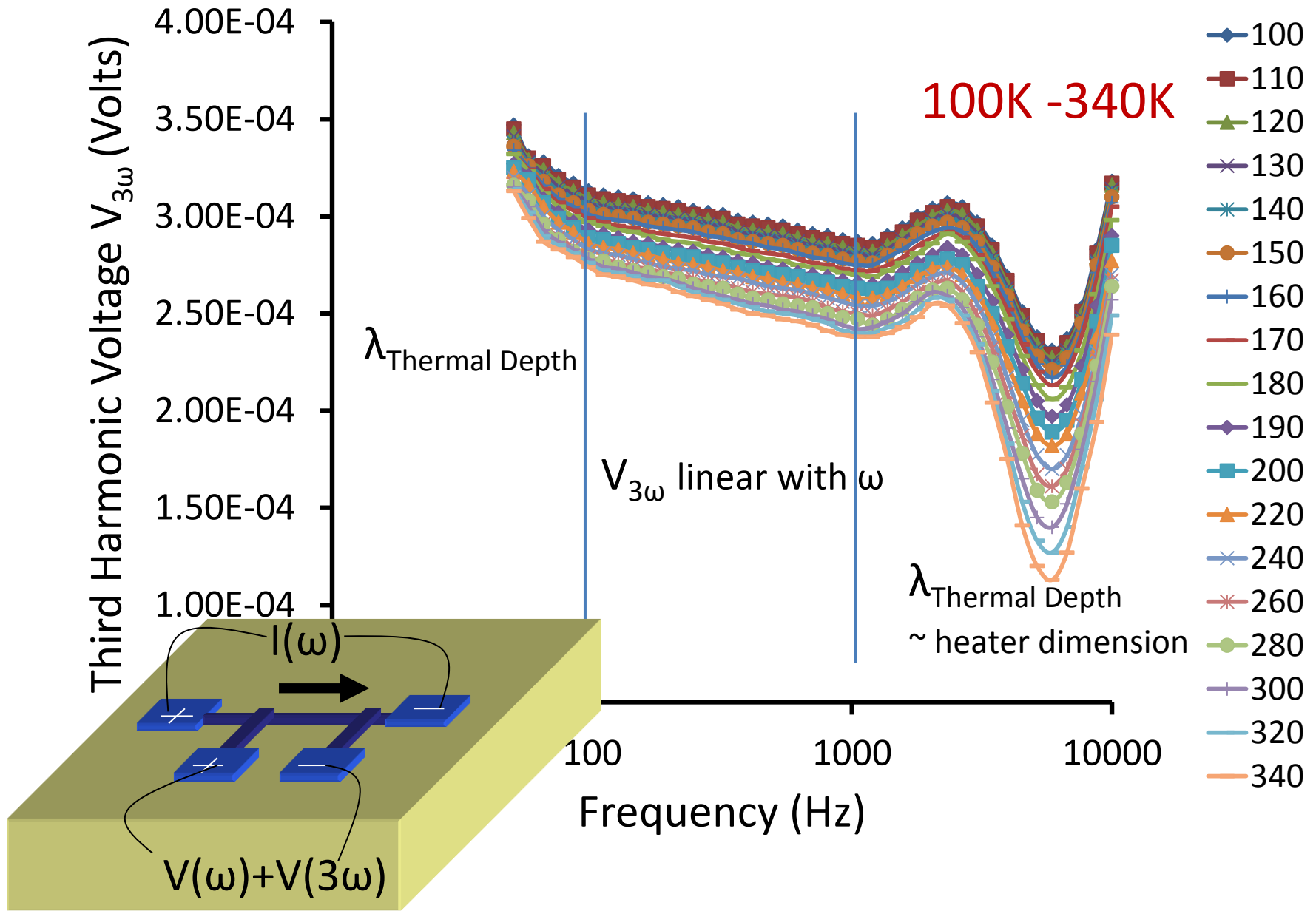
(contribution from both electrons and phonons)

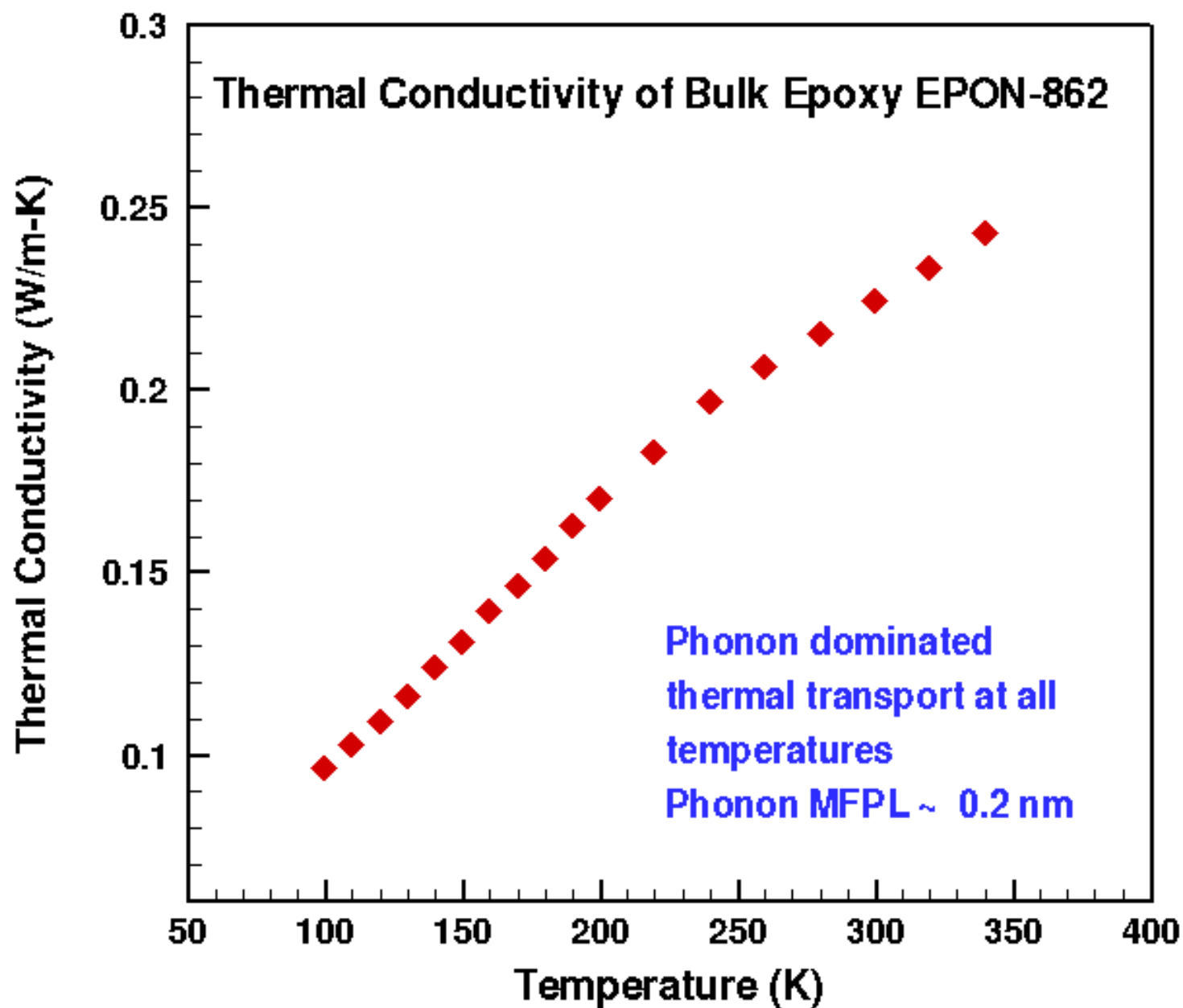


Phonon MFP
Room temp:
60 nm

Electron MFP
(bulk)
Room temp:
2.8 nm
Low temp:
25 nm

Thermal Conductivity of Bulk Epoxy (Epon-862)



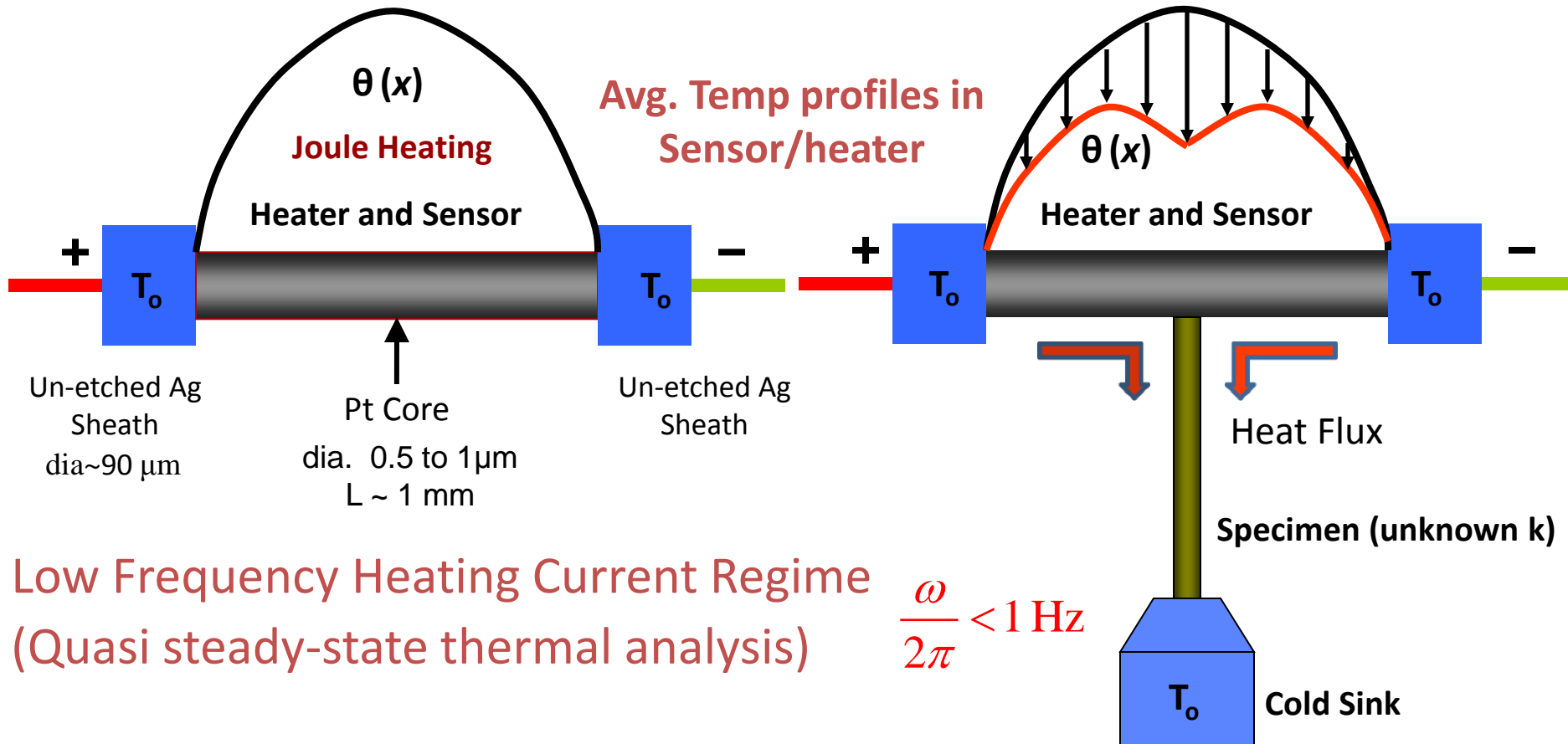


Thermal conductivity of Individual MWCNTs -- HOT WIRE PROBE

Wollaston wire (Ag/Pt)-- heater and sensing probe

(Along with $3\ \Omega$ method)

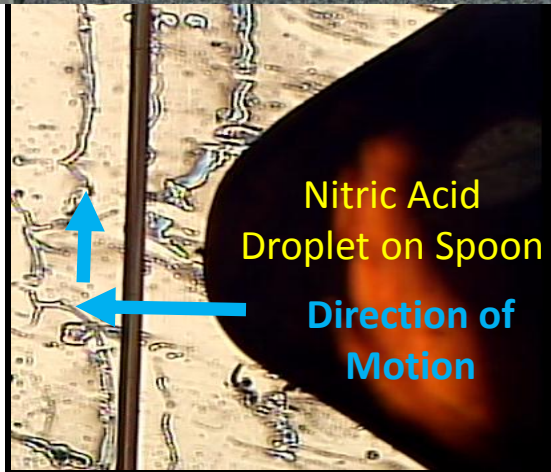
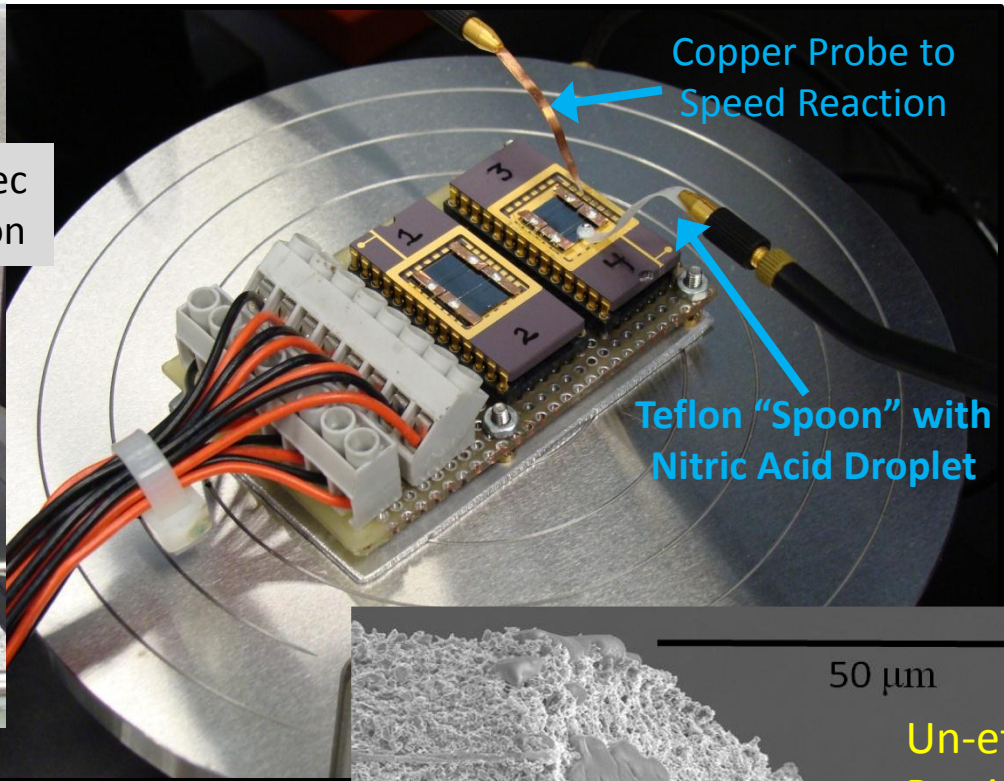
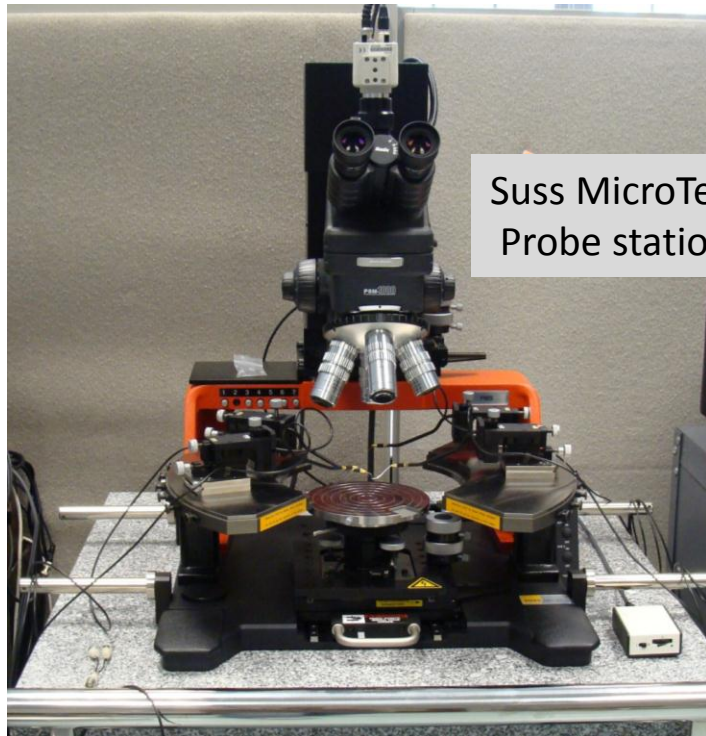
Sinusoidal current at ω leads to Joule heating in Pt. at 2ω ; Voltage measurements at ω and 3ω



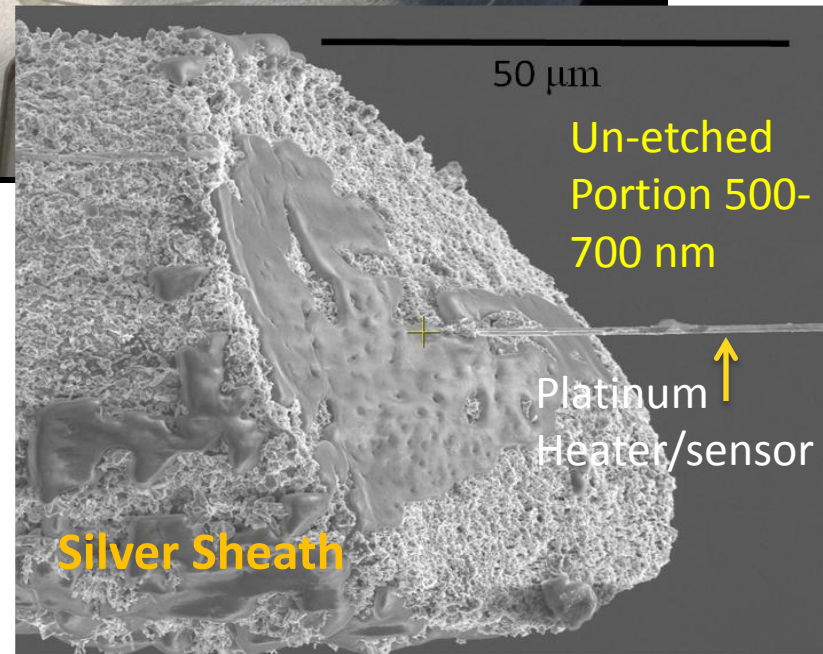
Low Frequency Heating Current Regime
(Quasi steady-state thermal analysis)

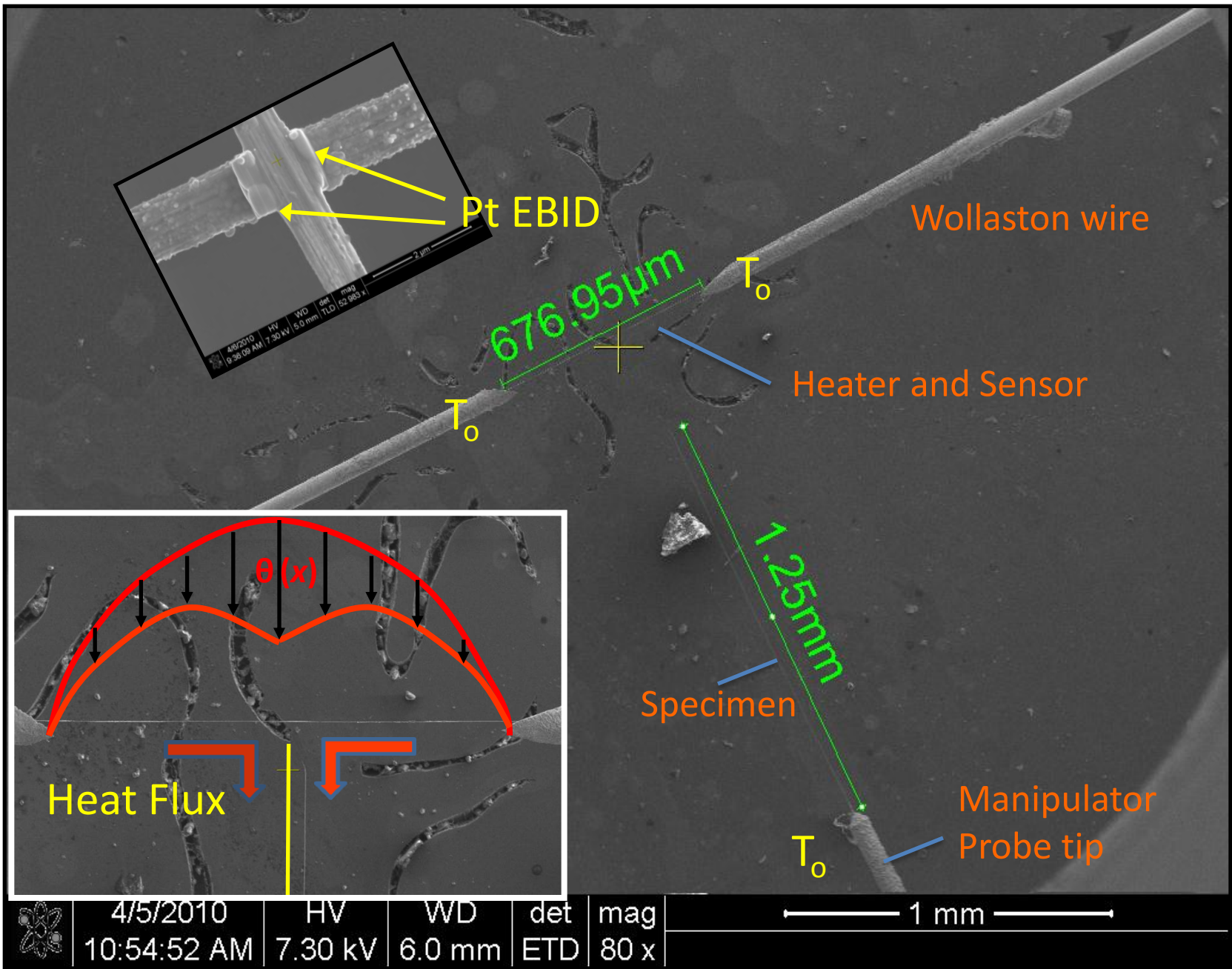
Change in average temperature -- Leads to a change in electrical resistance – leads to change in voltage at 3ω

Etching the Wollaston Wire— Platinum sensor/heater wire

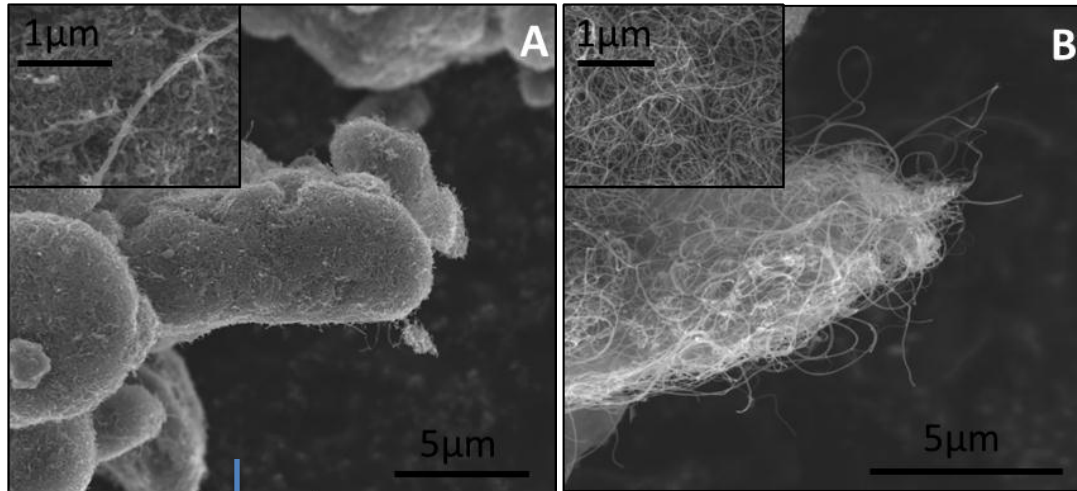


The copper and the teflon spoons are controlled using two micromanipulators in a Suss MicroTec probe station

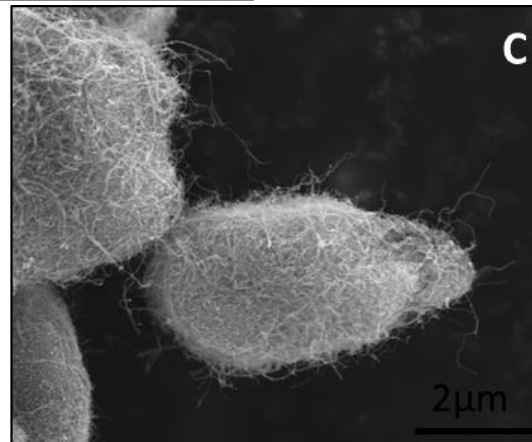




As-Received & Heat Treated (annealed) MWCNTs



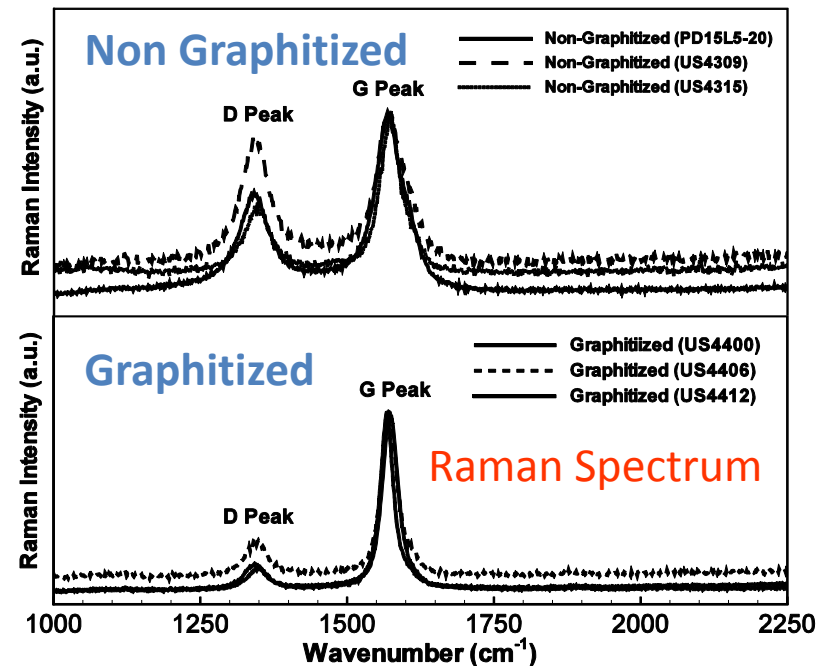
Non graphitized MWCNT
-- Nanolab Inc
-- US Nanomaterials Research



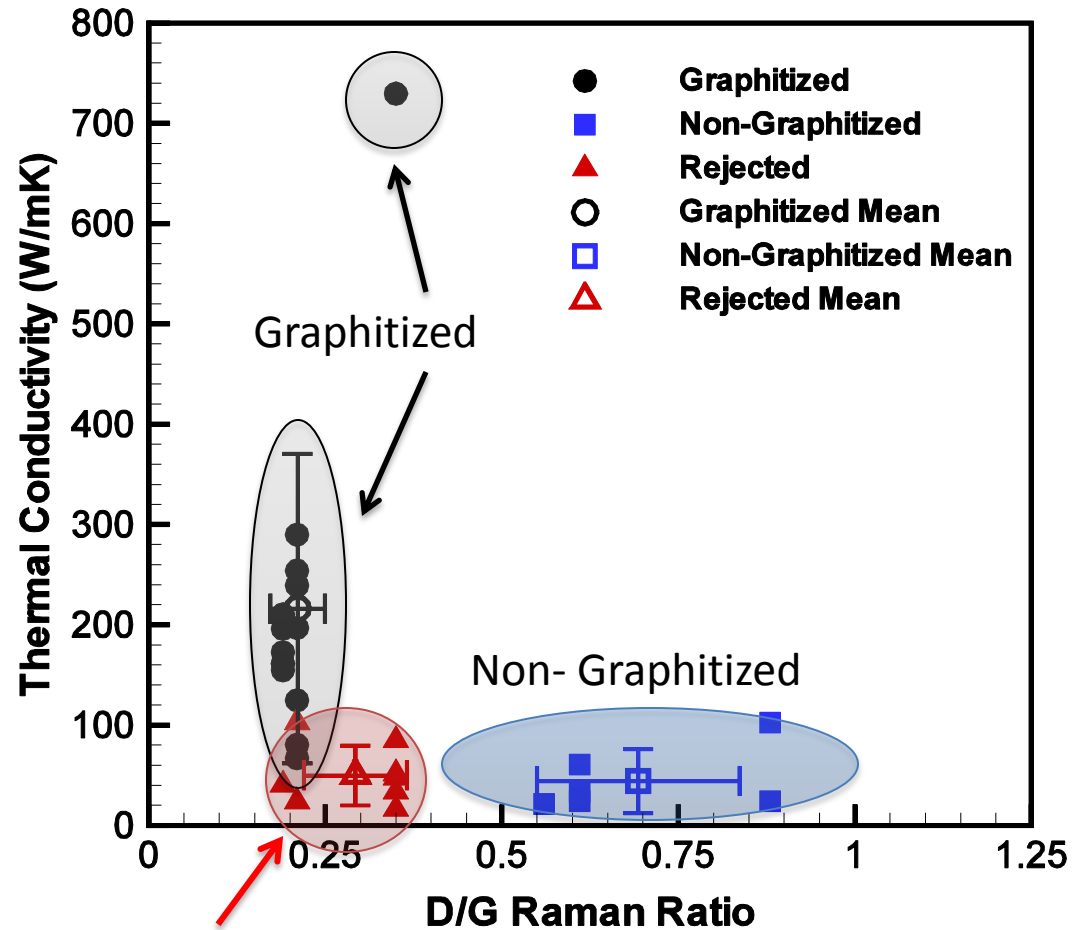
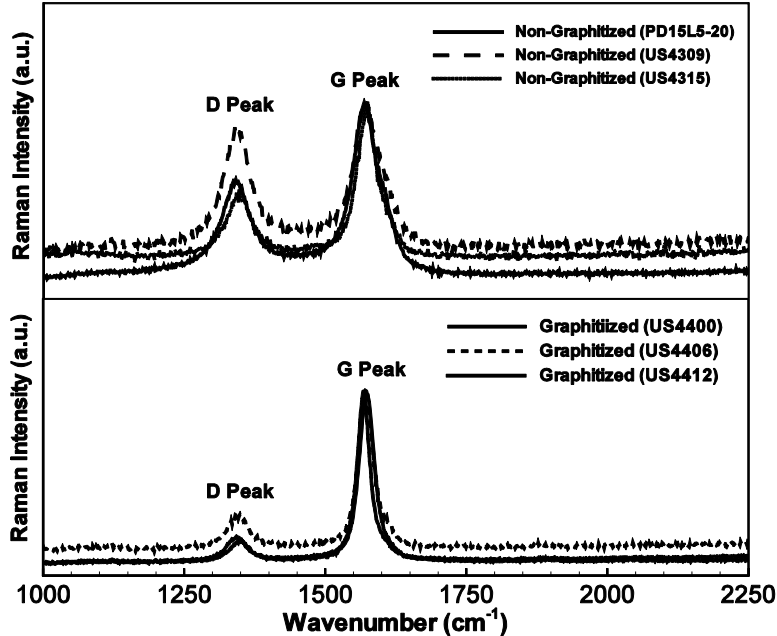
Graphitized MWCNT
- US Nanomaterials
Research

20 hour, 3000°C
Post-annealing heat
treatment

Smaller D/G ratio
Less number of defects

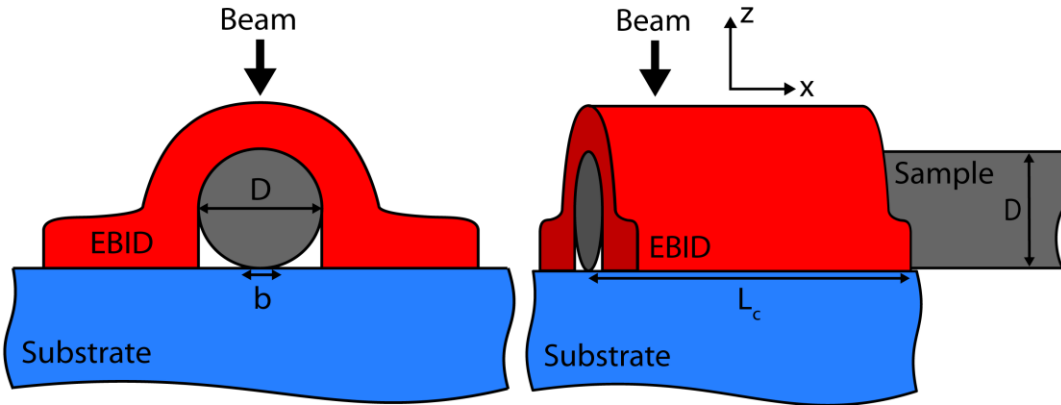


3 Ω Measurements on Individual MWCNTs



Graphitized but with morphological defects

Thermal Contact Resistance at the Pt wire-CNT Junction

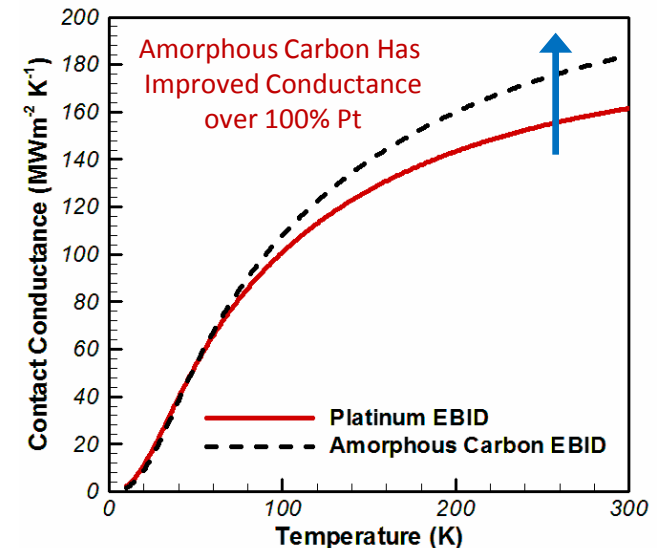
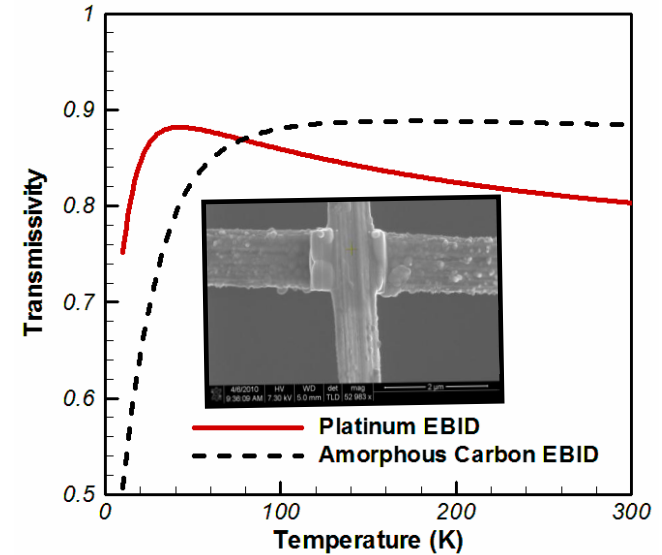


Required Information

- Phonon dispersion of EBID (Assume Debye Behavior since elastic properties have been measured⁴)
- Phonon dispersion of sample (Assume Graphite)
- Contact width (b) estimated from elastic properties assuming van der Waals forces of attraction
- Contact dimensions D, L_c are measured in SEM

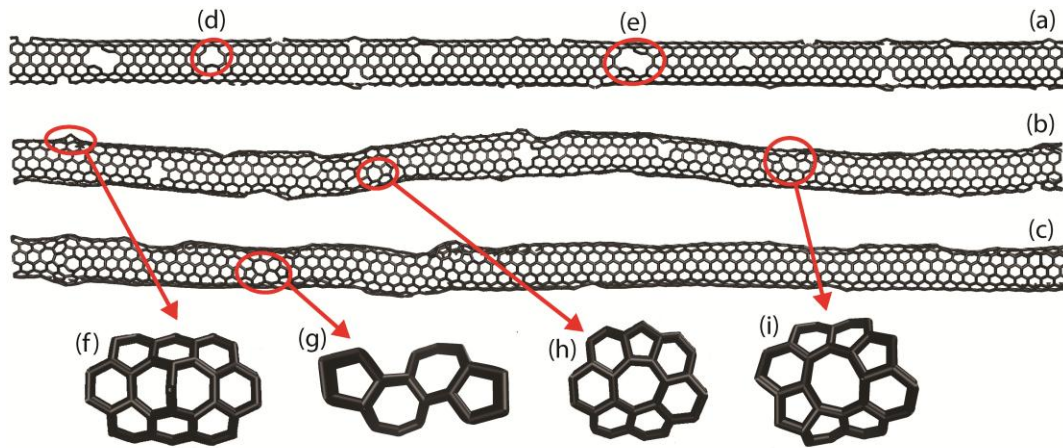
$$\alpha_{1-2} = \frac{\frac{1}{4} \sum_3 \int_{\omega} n \hbar \omega v_2 \text{DOS}_2(\omega) d\omega}{\frac{1}{2} \frac{1}{(2\pi)^2} \sum_{\alpha} \int_{k_z} \int_{k_r} n \hbar \omega v_{1z} k_r dk_r dk_z + \frac{1}{4} \sum_3 \int_{\omega} n \hbar \omega v_2 \text{DOS}_2(\omega) d\omega}$$

$$G_c = \frac{1}{R_c} = \frac{1}{2} \frac{1}{(2\pi)^2} \sum_{\alpha} \frac{d}{dT} \int_{k_z} \int_{k_r} \alpha_{1-2} n \hbar \omega v_{1z} k_r dk_r dk_z$$

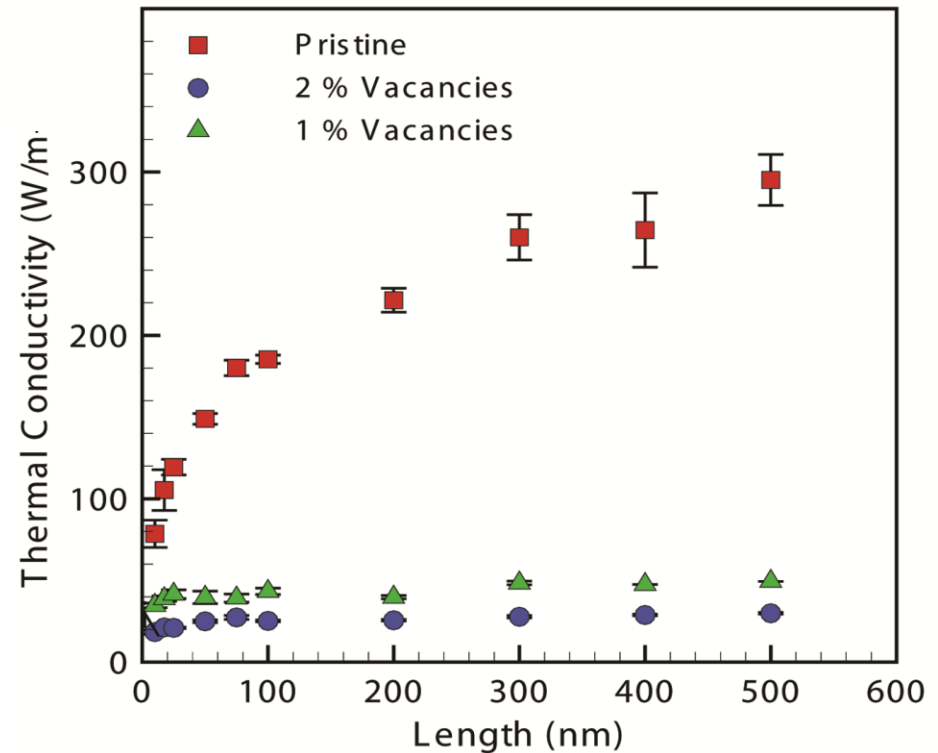


Correcting for contact conductance, k increases by 5% (Pt EBID)

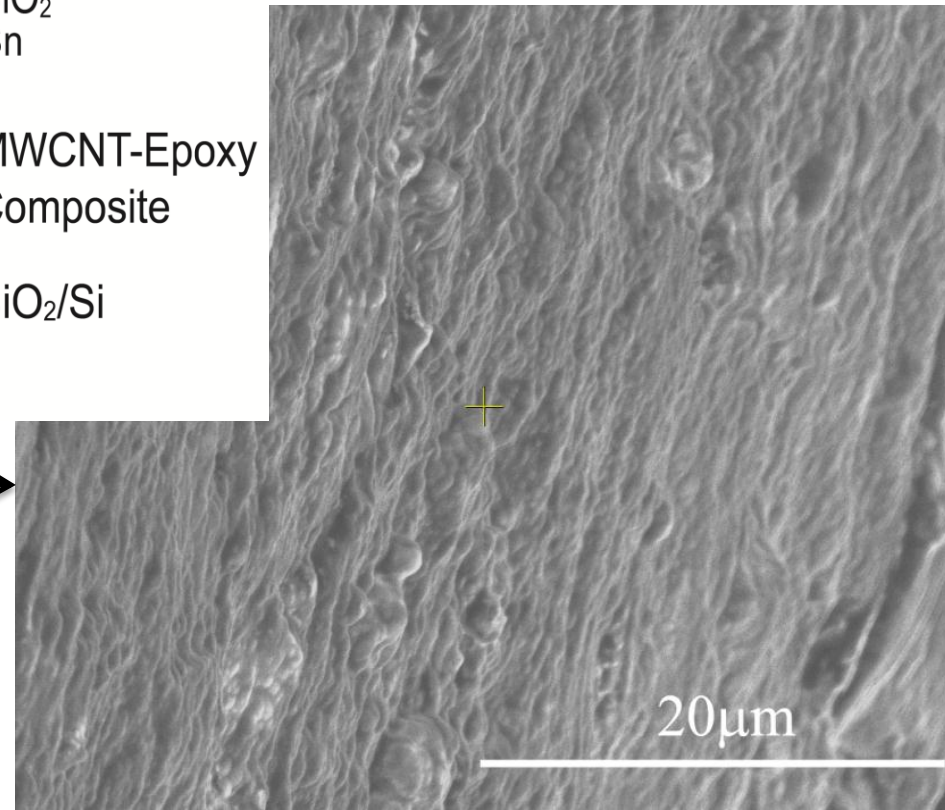
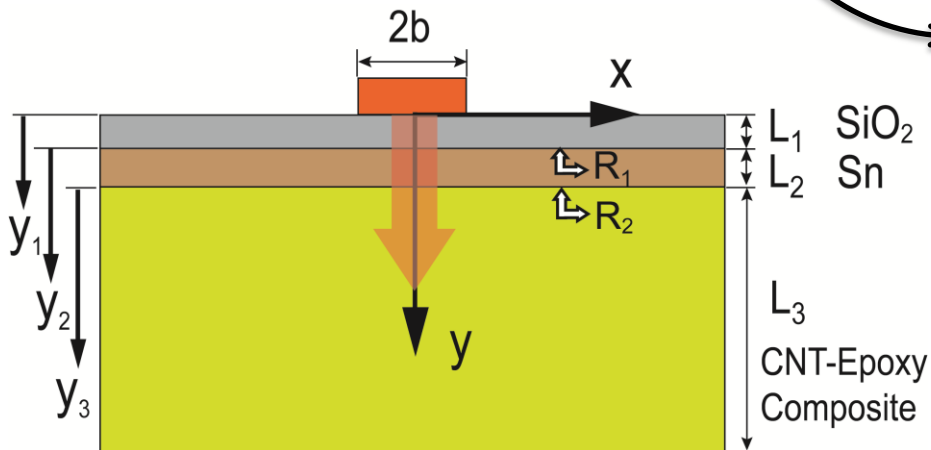
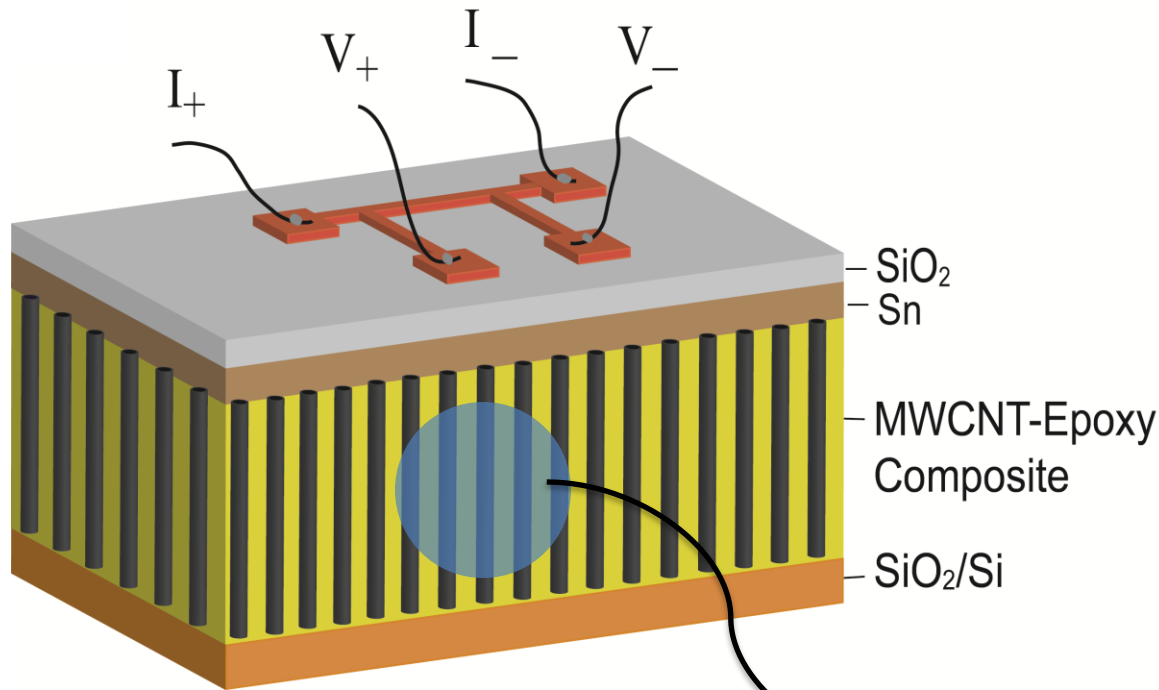
Molecular Dynamics: RNEMD



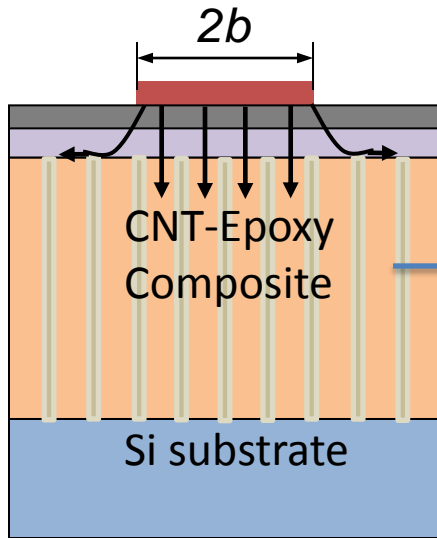
(6,6) armchair SWCNT
(with and without defects)



TIM Thermal Conductivity: 3Ω Method



TIM Thermal Conductivity: 3 Ω Experimental Results

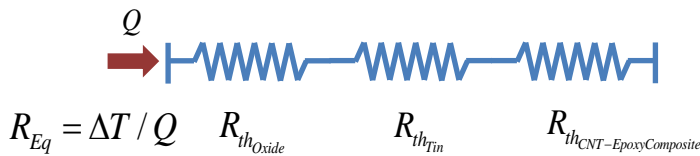


Sample	Thickness	Thermal Conductivity @ RT	Thermal Resistance (L/k)
Oxide	350 nm	1.1 W/m-K	3.18×10^{-7} K/W
Tin	500 nm	46 W/m-K	1.08×10^{-8} K/W
CNT-Epoxy	2.1 mm	5.77 W/m-K	3.64×10^{-4} K/W

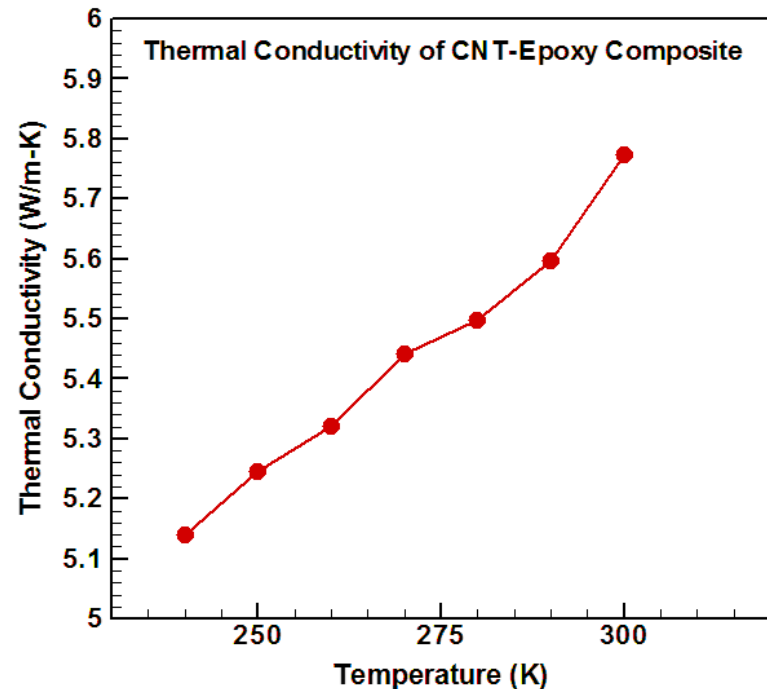
$$k_{system} = \frac{aV_{1W,rms}}{2\rho} \frac{Q_{avg}}{\ell} \frac{\ln(W_2 / W_1)}{V_{3W_1,rms} - V_{3W_2,rms}} \quad \text{MWCNTs } k \sim 60 \text{ W/m-K}$$

- SiO₂ 350 nm
- Sn 500 nm
- CNT-epoxy ~2.1 mm
- MWCNT 15-20 nm Dia
- Si 500 μ m

1D Resistance Network



$$\frac{L_{System}}{k_{System}} = \frac{L_{Oxide}}{k_{Oxide}} + \frac{L_{Tin}}{k_{Tin}} + \frac{L_{CNT-Epoxy}}{k_{CNT-Epoxy}}$$

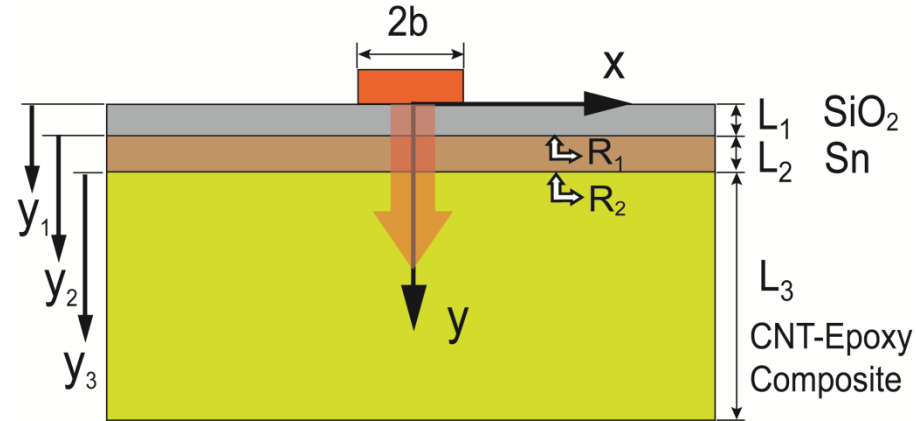


THERMAL MODEL (3 layer 1-D model)

$$T_j(y_j, t) = A.e^{(\eta_j y_j - i\omega t)} + B.e^{(-\eta_j y_j - i\omega t)}$$

$$\eta_j = \sqrt{-\frac{i\omega\rho_j C_{pj}}{k_{y,j}}} \quad \text{(Inverse of the penetration depth)}$$

$$q(y_1 = 0, t) = q_0 e^{-i\omega t} \quad \text{(Heat Flux)}$$



Thermal Impedance

$$g_j = k_{y,j} h_j$$

$$Z = \frac{T_1(0)}{q_0} = \frac{1}{\gamma_1} \left[\frac{\left(1 + \frac{\gamma_3}{\gamma_2} \eta_2 L_2\right) + \left(\frac{\gamma_3}{\gamma_1} + \frac{\gamma_2}{\gamma_1} \eta_2 L_2\right) \eta_1 L_1}{\left(1 + \frac{\gamma_3}{\gamma_2} \eta_2 L_2\right) \eta_1 L_1 + \left(\frac{\gamma_3}{\gamma_1} + \frac{\gamma_2}{\gamma_1} \eta_2 L_2\right)} \right] \quad \text{(without Interfacial resistance)}$$

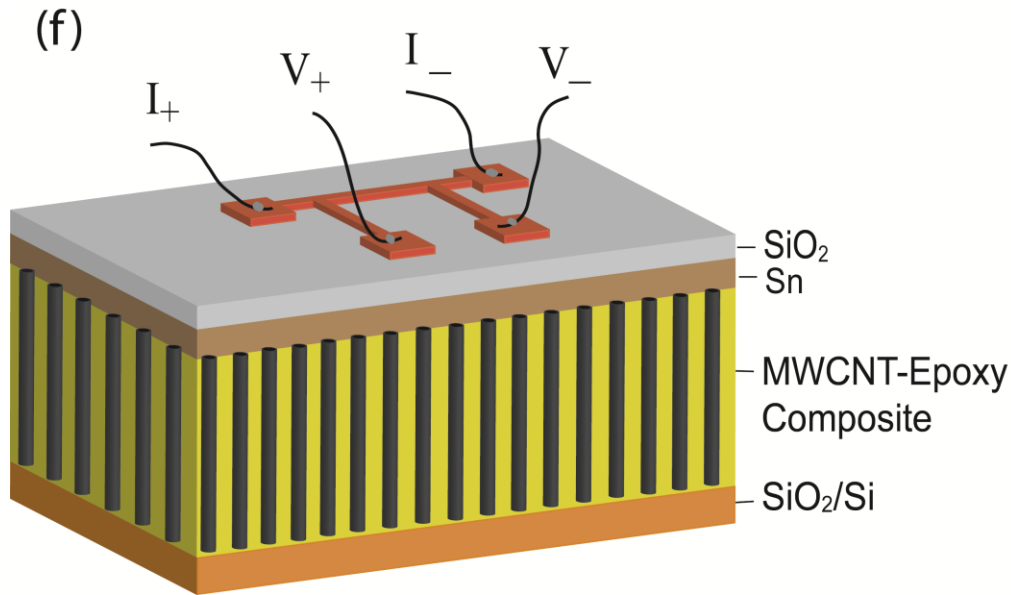
(with Interfacial resistance)

$$Z = \frac{1}{\gamma_1} \left[\frac{\left[\left(1 + \gamma_3 R_1 + \gamma_3 R_2\right) + \left(\gamma_2 R_1 + \frac{\gamma_3}{\gamma_2} + \gamma_2 \gamma_3 R_1 R_2\right) \eta_2 L_2 \right] + \left[\frac{\gamma_3}{\gamma_1} + \left(\frac{\gamma_2}{\gamma_1} + \frac{\gamma_2 \gamma_3}{\gamma_1} R_2\right) \eta_2 L_2 \right] \eta_1 L_1}{\left[\left(1 + \gamma_3 R_1 + \gamma_3 R_2\right) + \left(\gamma_2 R_1 + \frac{\gamma_3}{\gamma_2} + \gamma_2 \gamma_3 R_1 R_2\right) \eta_2 L_2 \right] \eta_1 L_1 + \left[\frac{\gamma_3}{\gamma_1} + \left(\frac{\gamma_2}{\gamma_1} + \frac{\gamma_2 \gamma_3}{\gamma_1} R_2\right) \eta_2 L_2 \right]} \right]$$

R_1 = Thermal resistance between SiO₂ and Sn

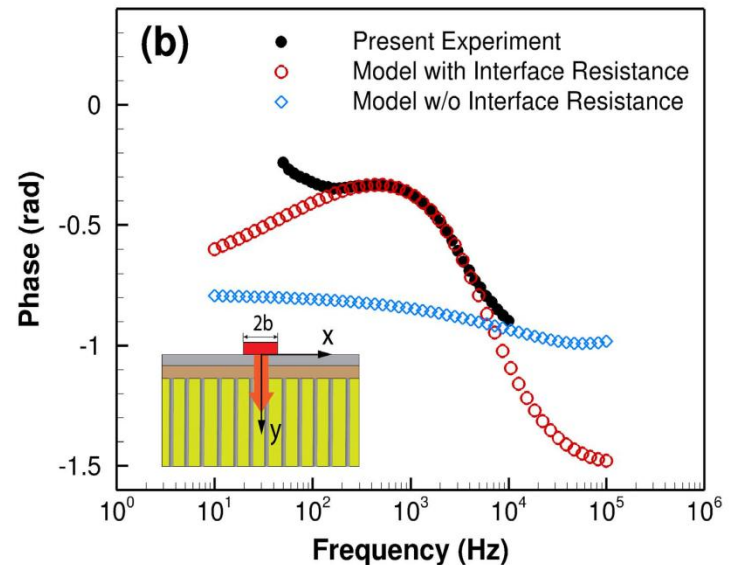
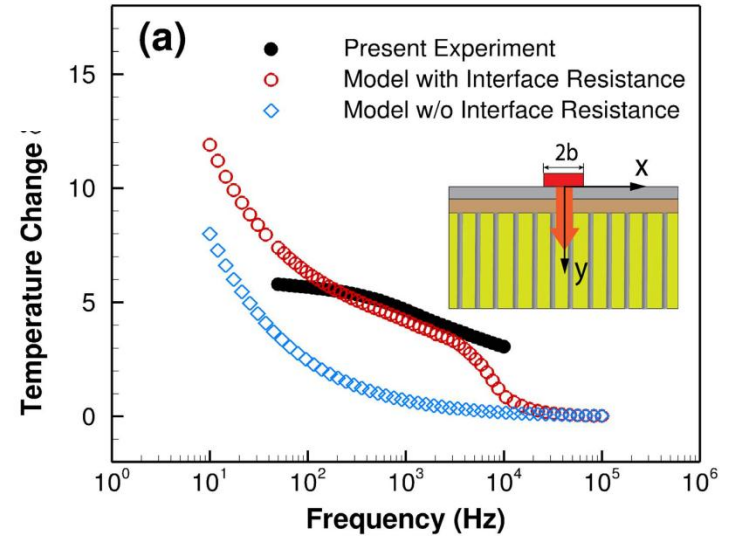
R_2 = Thermal resistance between Sn and MWCNT

Estimate Interfacial Thermal Resistance



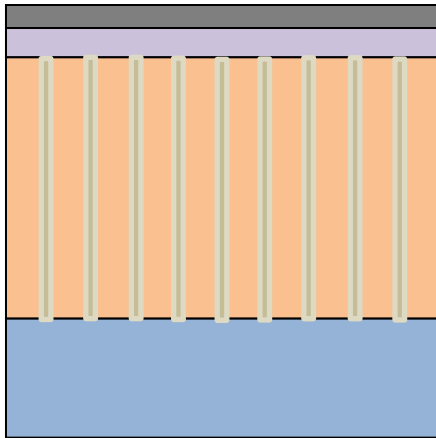
Thermal Interface Resistance between oxide and tin -- $5 \times 10^{-5} \text{ m}^2 \text{ K/W}$

Thermal Interface Resistance between tin and VA MWCNT -- $8 \times 10^{-6} - 8.5 \times 10^{-7} \text{ m}^2 \text{ K/W}$



Estimate of Composite Thermal Conductivity based on the Rule of Mixtures

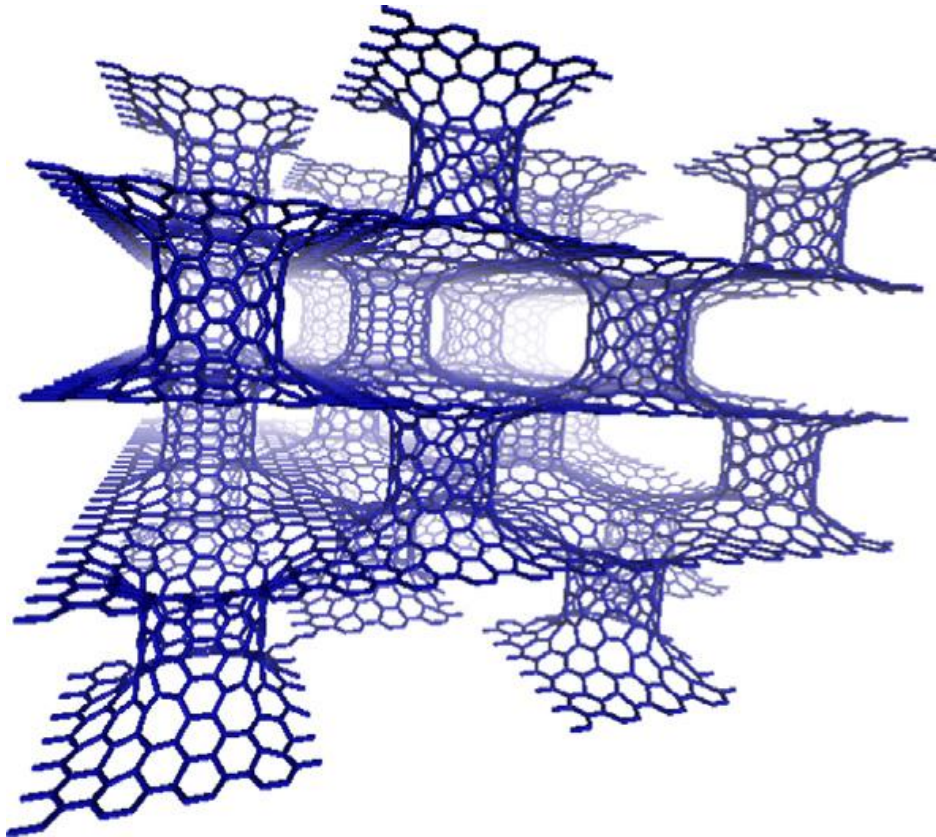
$$k_{Eff} = k_{Air} f_{Air} + k_{Epoxy} f_{Epoxy} + k_{CNT's} f_{CNT's}$$



Sample 10 X 11.5 X 2.1 (mm)	Weight %	Density Kg /m ³	Volume %	Thermal Conductivity
Carbon Nanotubes	12.91%	694	9.726%	60 W/m-K (<i>measured</i>)
Epoxy	86.97%	1090	41.764%	0.234 W/m-K (<i>measured</i>)
Air	0.11%	1.2	48.51%	0.026 W/m-K
CNT-Epoxy Composite				5.77 W/m-K (Measured) 5.95W/m-K (predicted)

USE GRAPHITIZED VA MWCNT ARRAYS -- Can Push $K_{TIM} \sim 20 \text{ W}/(\text{m-K})$

3-D TIMS: Pillared Graphene-CNT Networks



Provides avenues for both in-plane and cross-plane thermal conductivity

- Inter-pillar distance
- Pillar length
- CNT-graphene nodes (junctions)

