



AFOSR Grantees'/Contractors' Meeting

Mechanics of Multifunctional Materials & Microsystems



Multifunctional Hybrid Composites for Thermal Materials

Task: 2302BL

Dr. Les Lee, Program Manager

03 August 2012

Arlington, VA

**Ajit Roy, Chris Muratore, Sergei Shenogin,
Sabyasachi Ganguli, Jay Lee, Vikas Varshney**

Integrity ★ Service ★ Excellence

**Materials & Manufacturing Directorate
Air Force Research Laboratory**



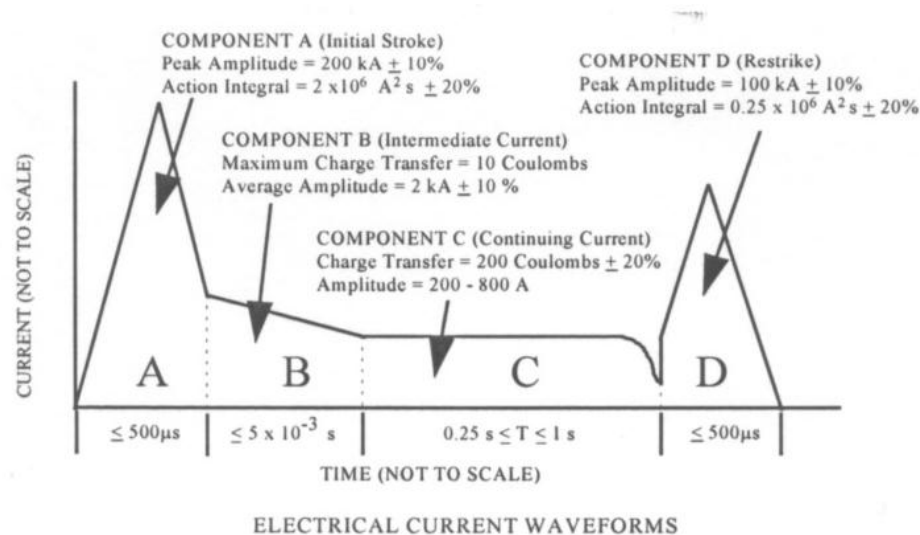
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Why Conductive Composites?

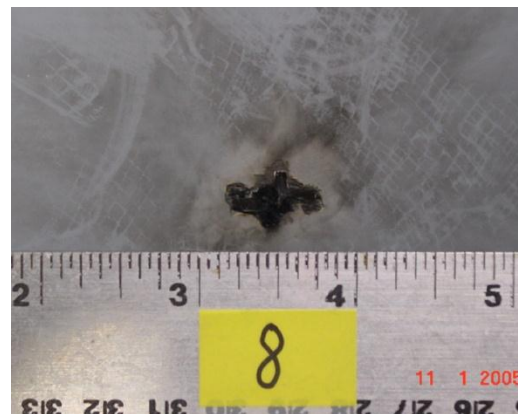


- Lightning strike related damage
 - Peak amplitude ~ 200 kA
 - Duration $\sim 500\mu\text{s}$



Ref: MtL-STD-1757A

- Protection against laser (DE weapons)
 - 290 W/cm^2 shot chars paint and melts Al in 0.5 sec



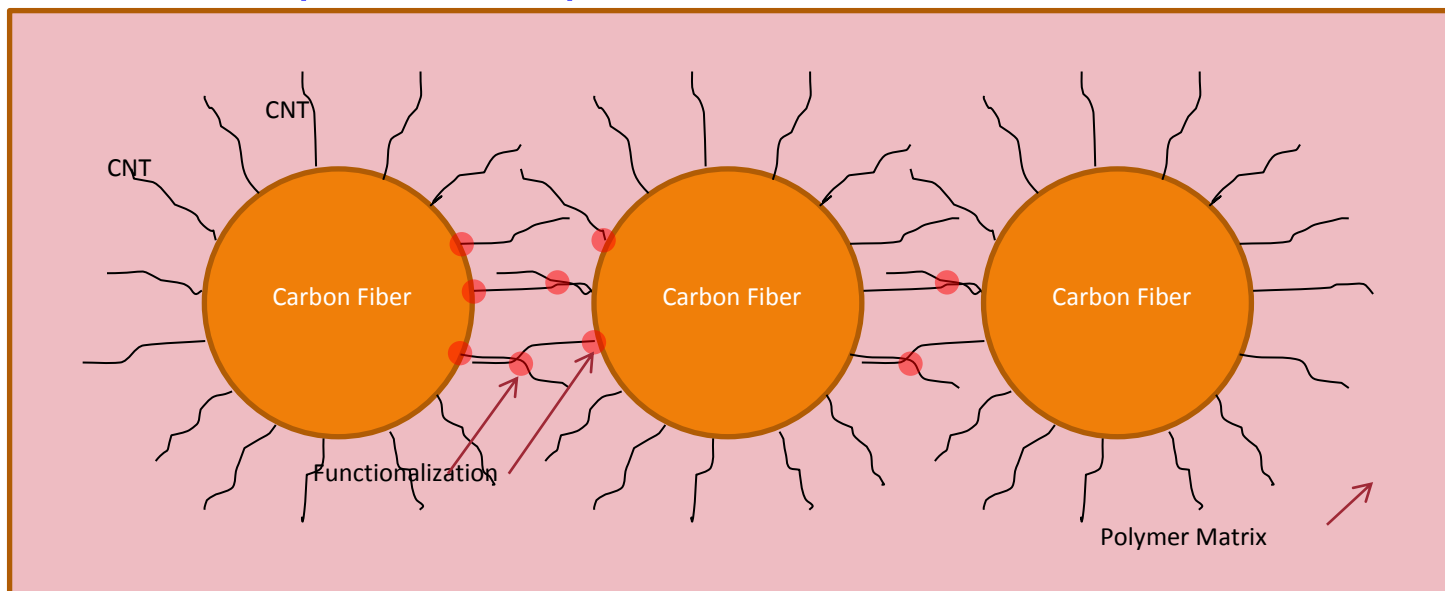
Ref: Fielding, et al, SAMPE, 2005





Overall Objective

- Hierarchical carbon fiber morphology for tailored thermal properties in heterogeneous materials systems
 - Fiber reinforced composites
 - Sensors, Heat sink, etc.



Achieving the appropriate thermal interface morphology is essential
Interfaces: CNT-CNT; CNT-polymer; CNT-carbon fiber



Technical Progress

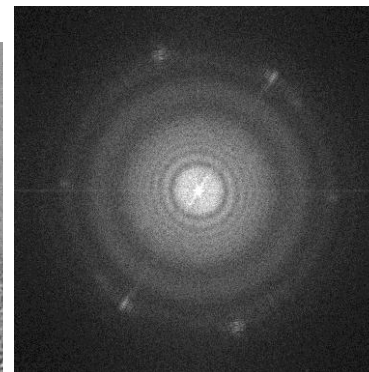
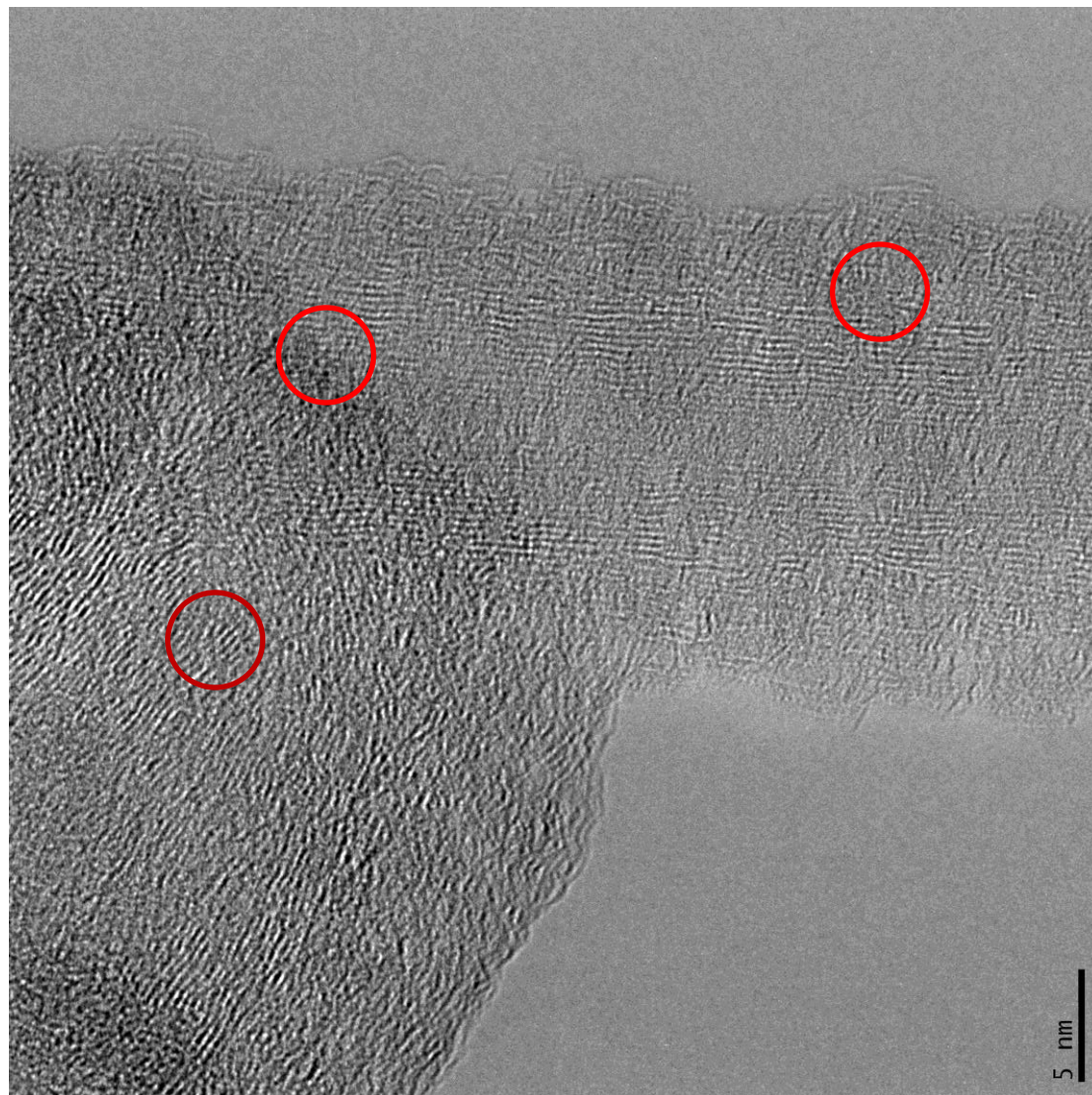
This year...



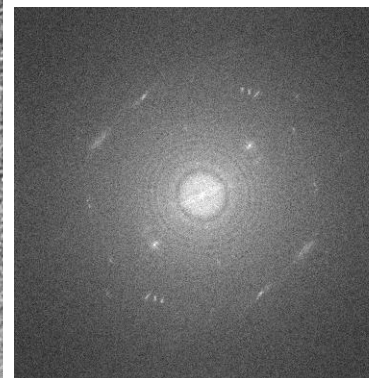
- Wave Packets – single mode phonon transmission in functionalized CNT - [J. Chem Physics, 135, 104109 \(2011\)](#)
- Kapitza resistance – Boltzmann-Peierls-Callaway equation – a mesoscale computational tool - [Physical Review E, 83, \(2011\)](#)
- Thermal rectification in asymmetric 3D nanostructure - [Nano Letters, 2012](#)
- Thermal conductivity reduction through helical nanowire superlattice structure (thermoelectrics) - [Nanoscale, 2012, 4, 5009](#)
- Thermal interface: a review - [ACS Applied Mater. Interfaces, 4 \(2\), 2012](#)
- **Metal – CNT interface**
 - MD simulation, processing, measurements



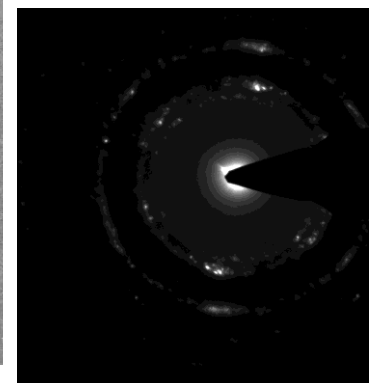
MWCNT Graphite Interface (Hexagonal Crystal ED Patterns)



Nanotubes



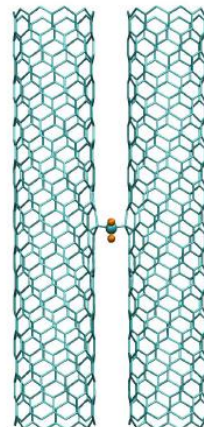
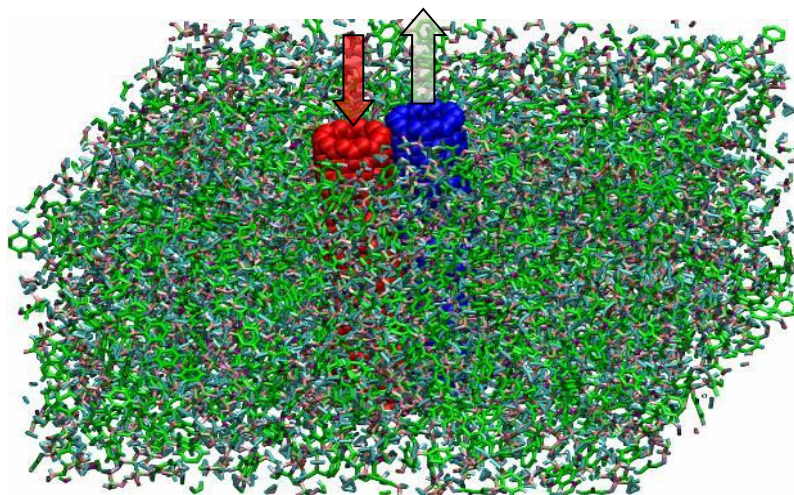
Substrate



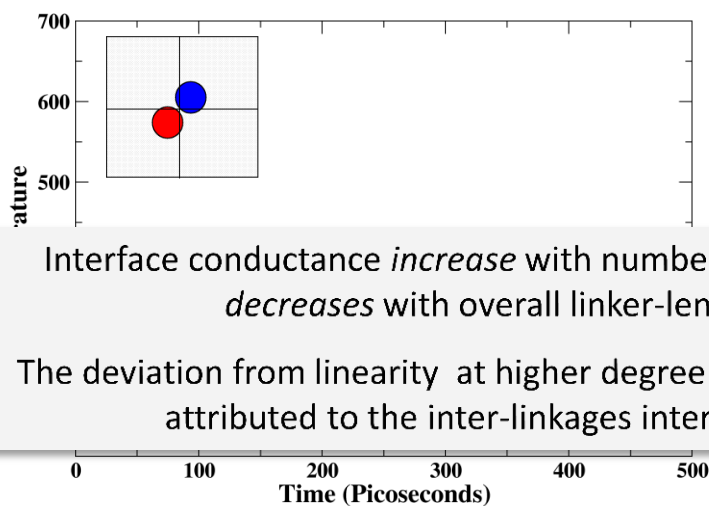
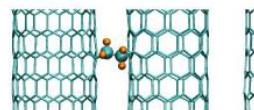
Interface



Interface Thermal Resistance across CNTs: Transverse Connection with Polymer Molecules

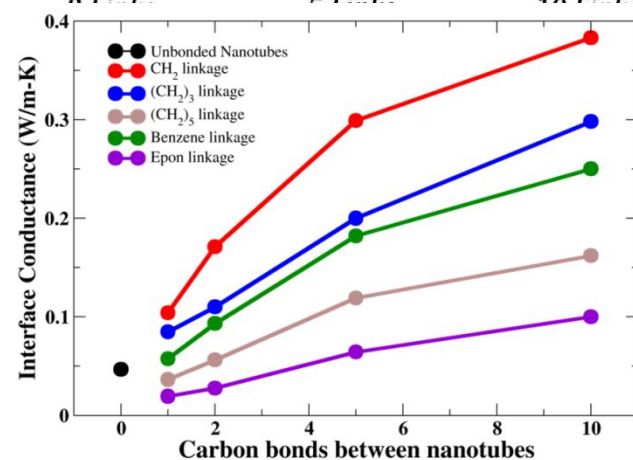
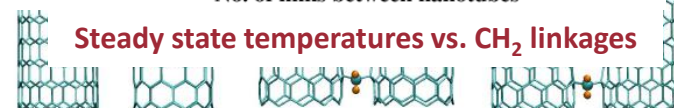
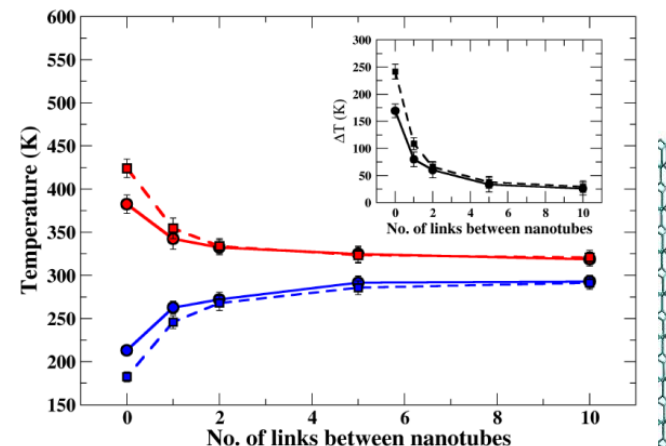


1 Link



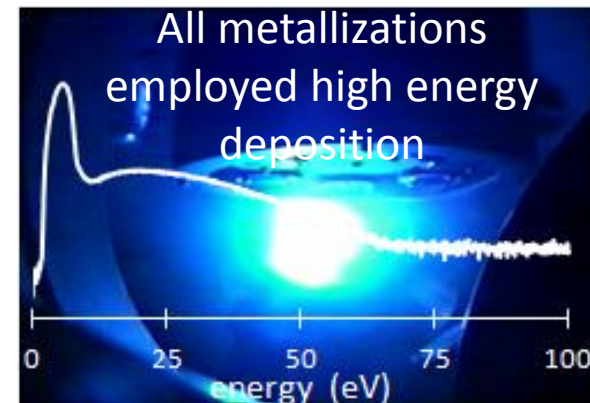
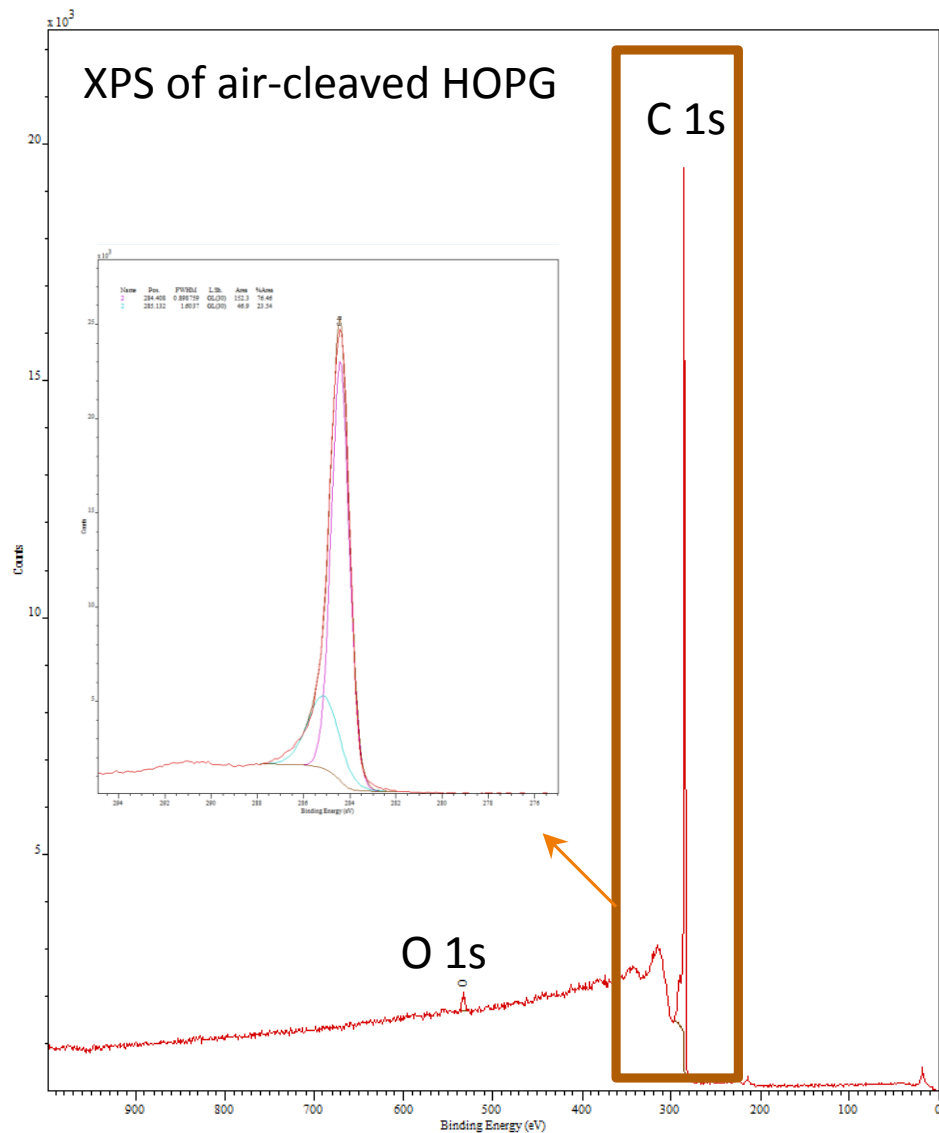
Interface conductance *increase* with number of linkages but *decreases* with overall linker-length.

The deviation from linearity at higher degree of functionality is attributed to the inter-linkages interactions.

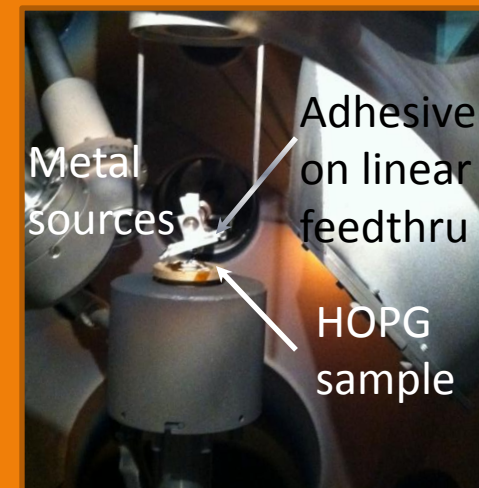




Effects of Ambient Environment During Cleaving on Interfacial Chemistry

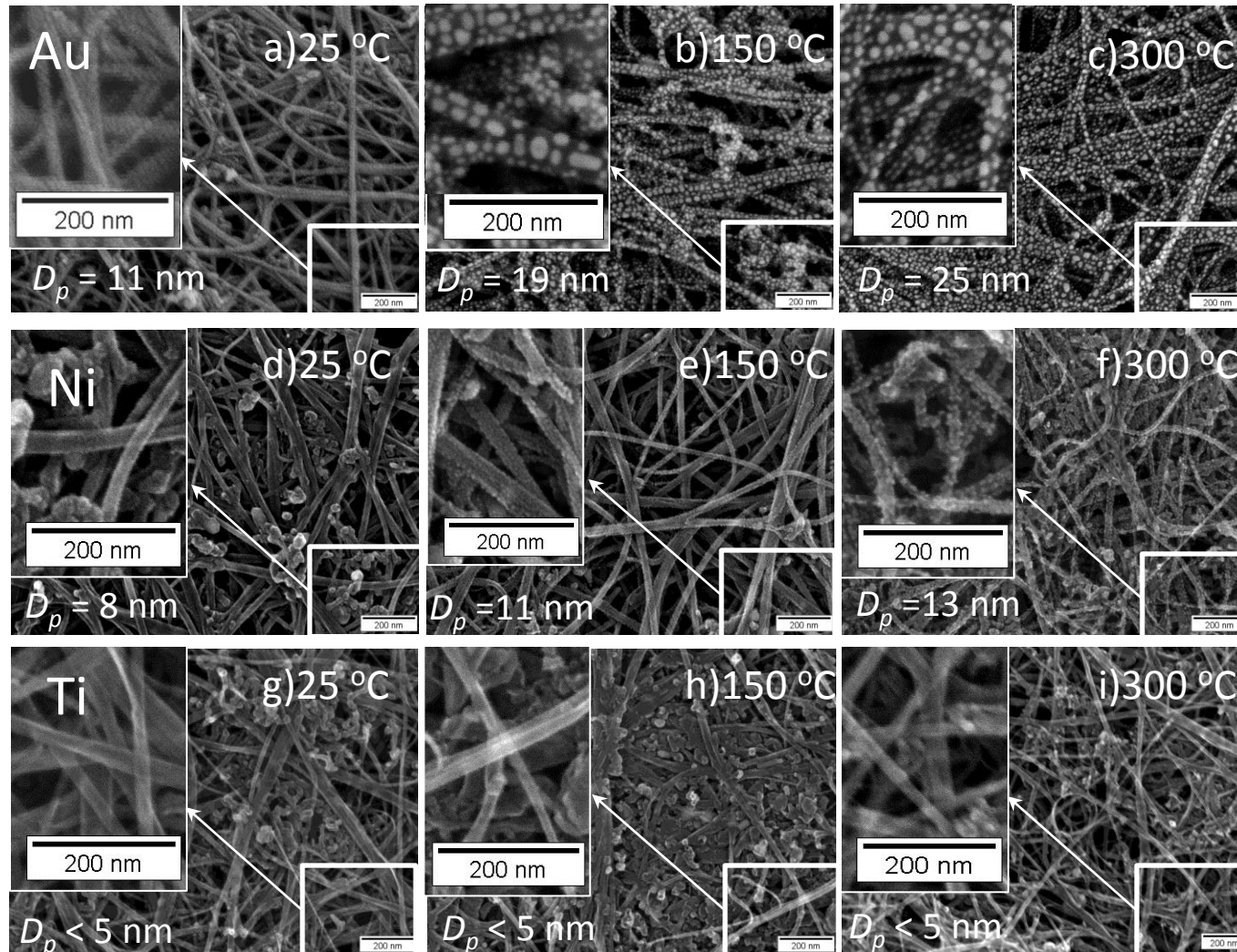


Vacuum cleaving apparatus





Intrinsic Factors Affecting Particle Morphology



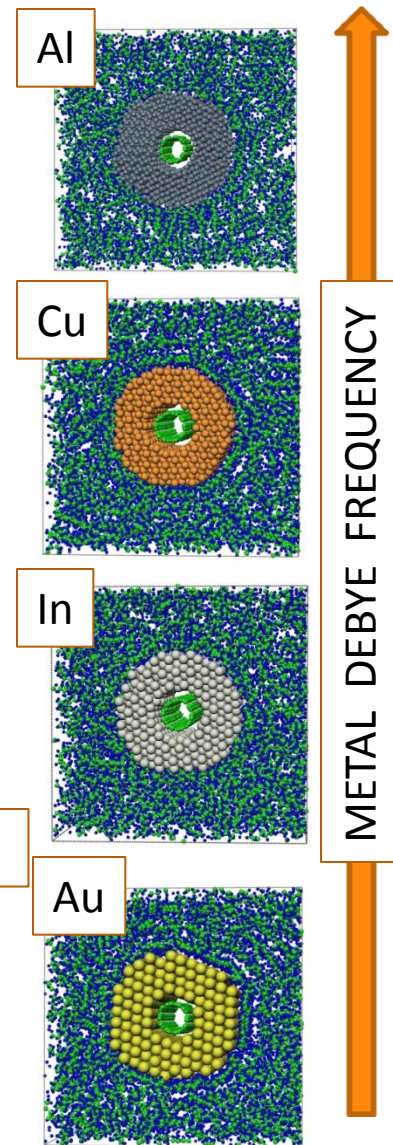
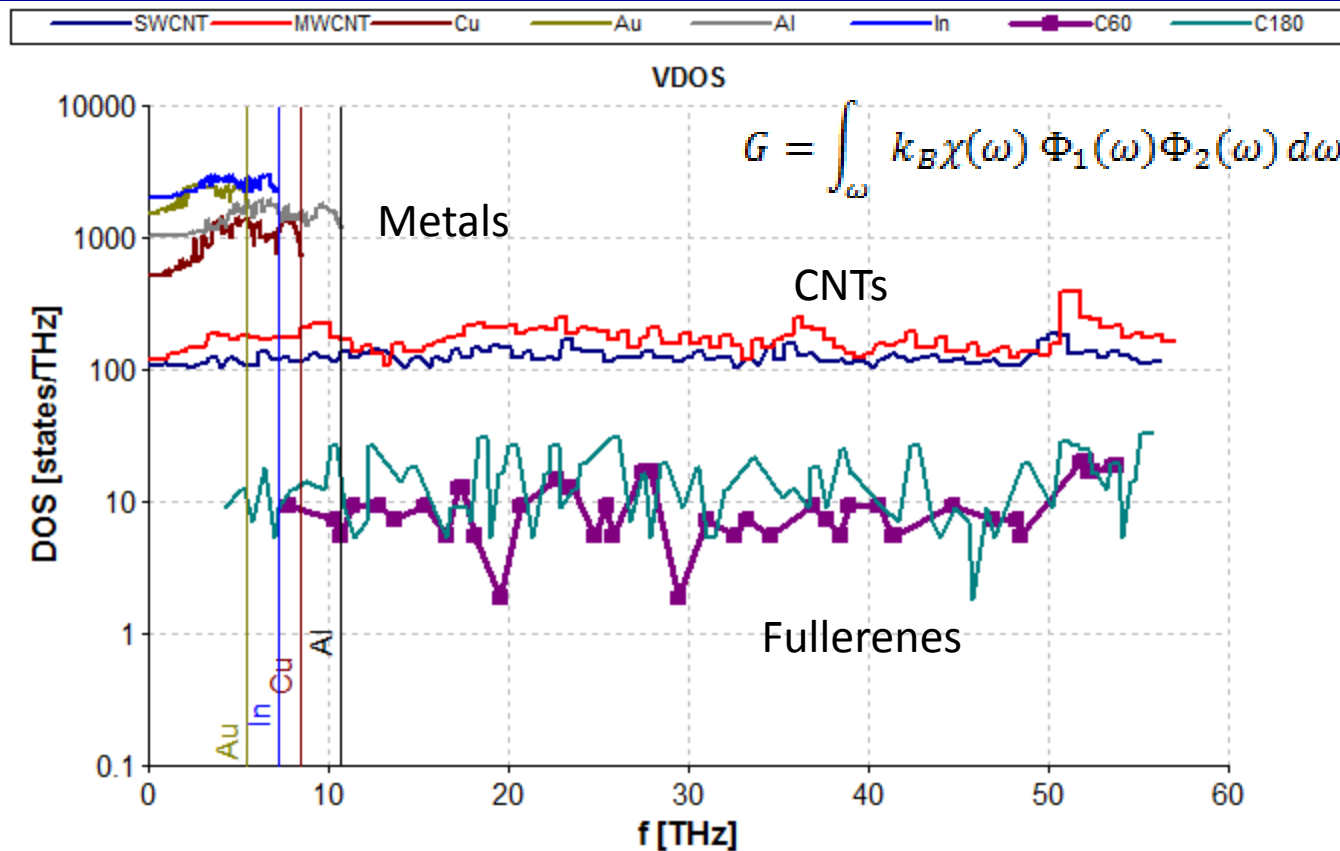
Increasing
cohesive
energy of
metal



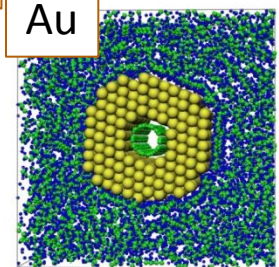
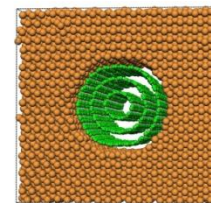
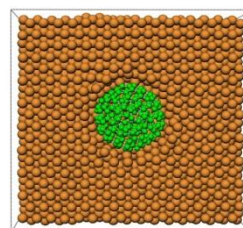
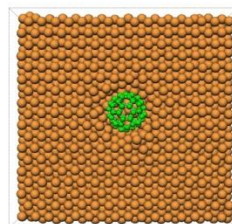
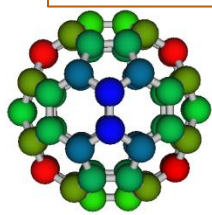
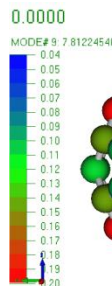
Increasing
particle
size



Simulation Approach: models of soft and hard carbon structures in metal matrix

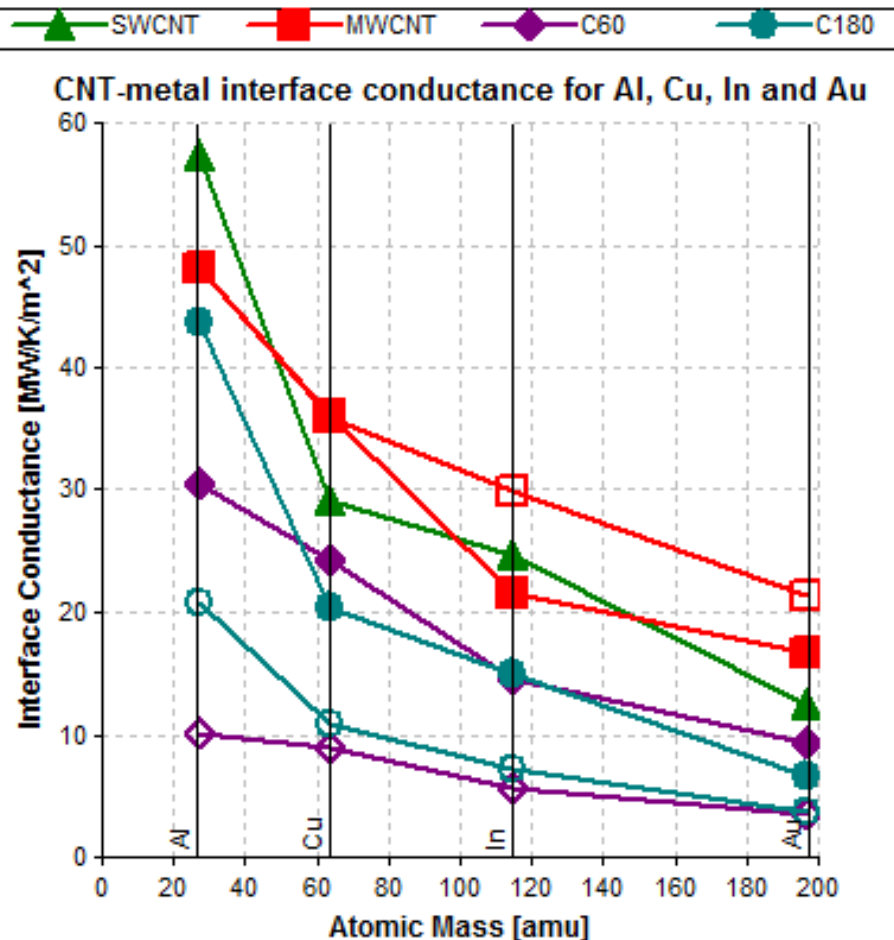


•No (or narrow) overlap in fullerene / metal vibrational spectra





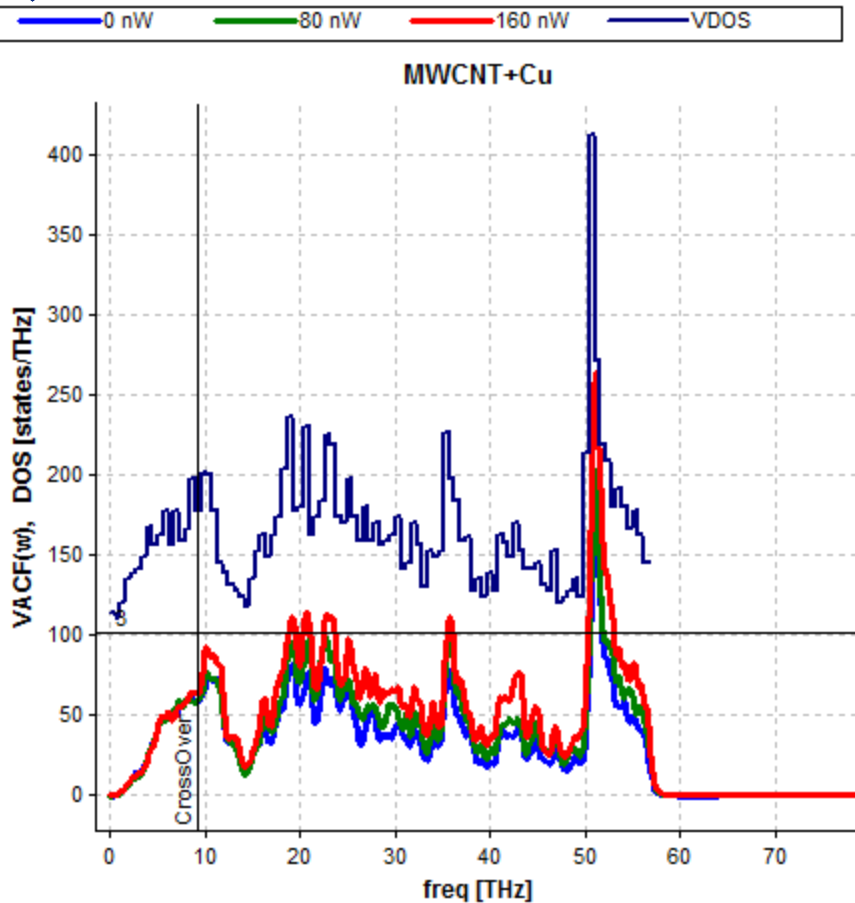
Conductance for Different Carbon-Metal Interfaces in NEMD Simulations



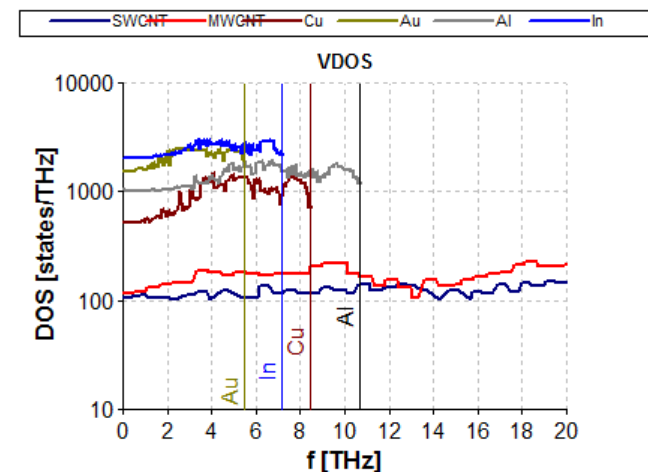
- Values are low (metal-metal 300-1000 MW/m²/K)
- Similar conductance found for MWCNT and SWCNT interfaces
- Conductance is higher for lighter metal
- CNT interfaces show similar conductance in active heating and temperature relaxation modes
- Lowest conductance is for C₆₀/Gold interface in temperature relaxation mode (~3.5 MW/m²/K)
- C₆₀/polymer without coating ~12..15 MW/m²/K)



Energy of vibrational modes in NEMD – MWCNT in Cu



- The peaks of $F(w)$ correspond to VDOS obtained from the vibrational analysis
- There is a sharp transition near Debye frequency of copper (~ 8.5 THz): vibrational modes at lower frequencies are “cold”
- Interfacial conductance is proportional to the “overlap” between VDOS of metal and CNT – diffuse mismatch model works



$$C(t) = \langle \vec{v}(t) \cdot \vec{v}(0) \rangle$$

$$F(\omega) = \frac{1}{2\pi} \int_0^\infty C(t) e^{-i\omega t} dt$$

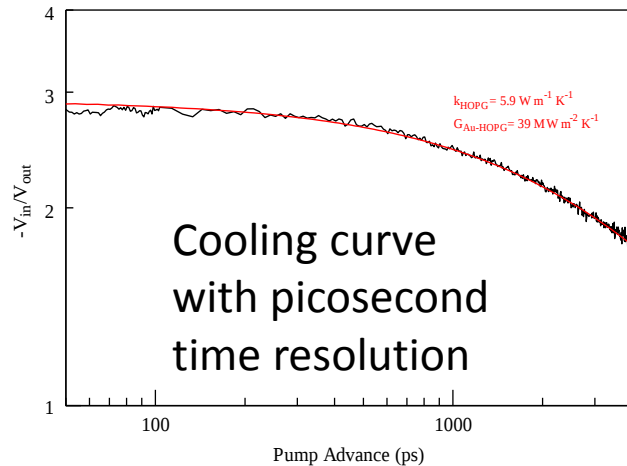




Interface Conductance Measurements with Time Domain Thermal Reflectance (TDTR)



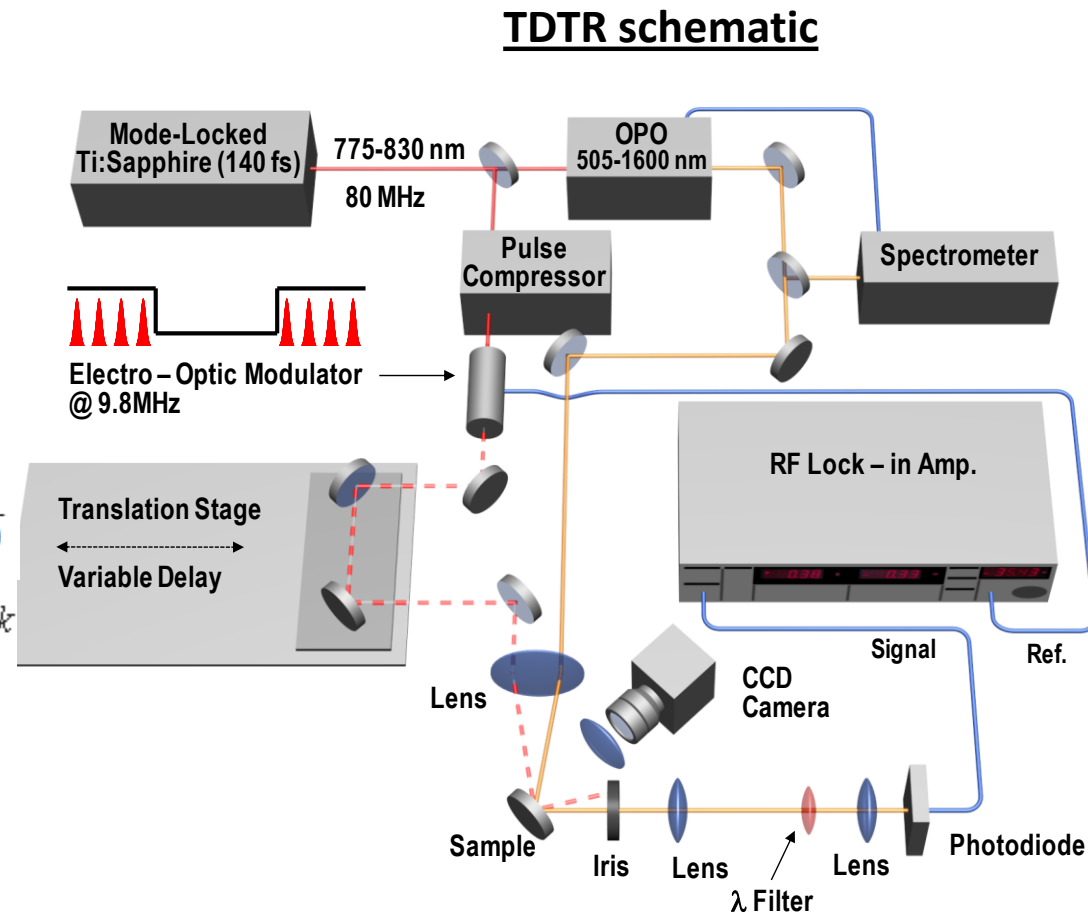
Au-HOPG "121911a"



$$-\frac{V_{in}}{V_{out}} = \frac{\sum_{-m}^m (\Delta T(m/\tau + f) + \Delta T(m/\tau - f)) \exp(i2\pi mt/\tau)}{i \sum_{-m}^m (\Delta T(m/\tau + f) - \Delta T(m/\tau - f)) \exp(i2\pi mt/\tau)}$$

$$\Delta T = 2\pi A \int_0^\infty G(k) \exp(-\pi^2 k^2 (w_0^2 + w_1^2)/2) k dk$$

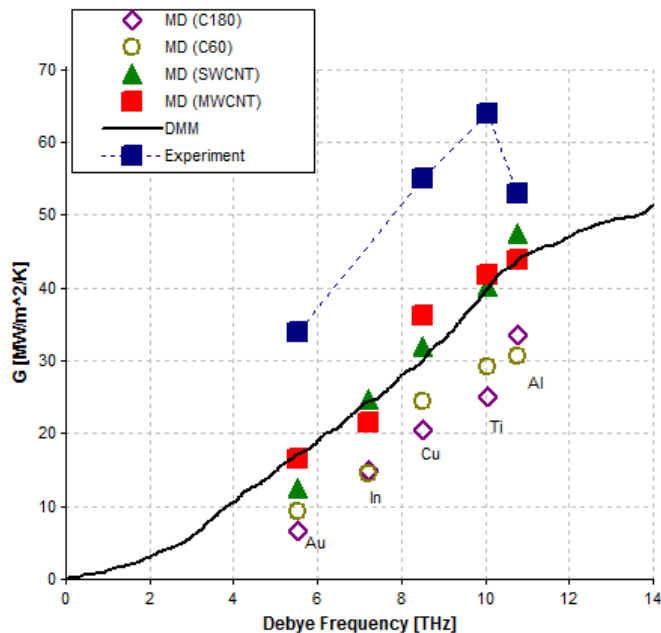
Undoubtedly the best technique for measurement of interface conductance, but requires $R_a < 25 \text{ nm}$!



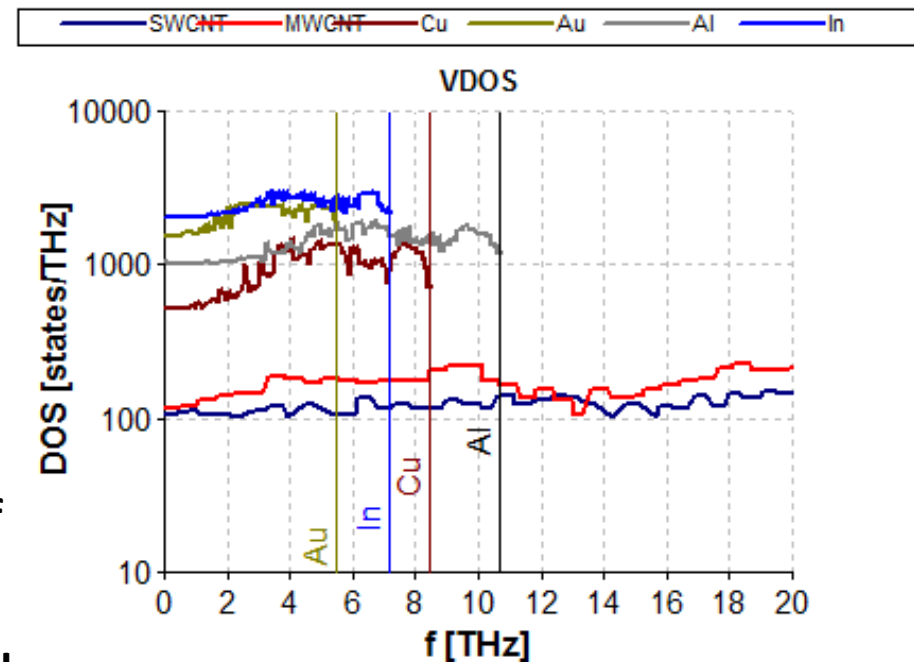
(No way for nanotube-based materials!)



MD conductance for graphite-metal interface: well explained by DMM



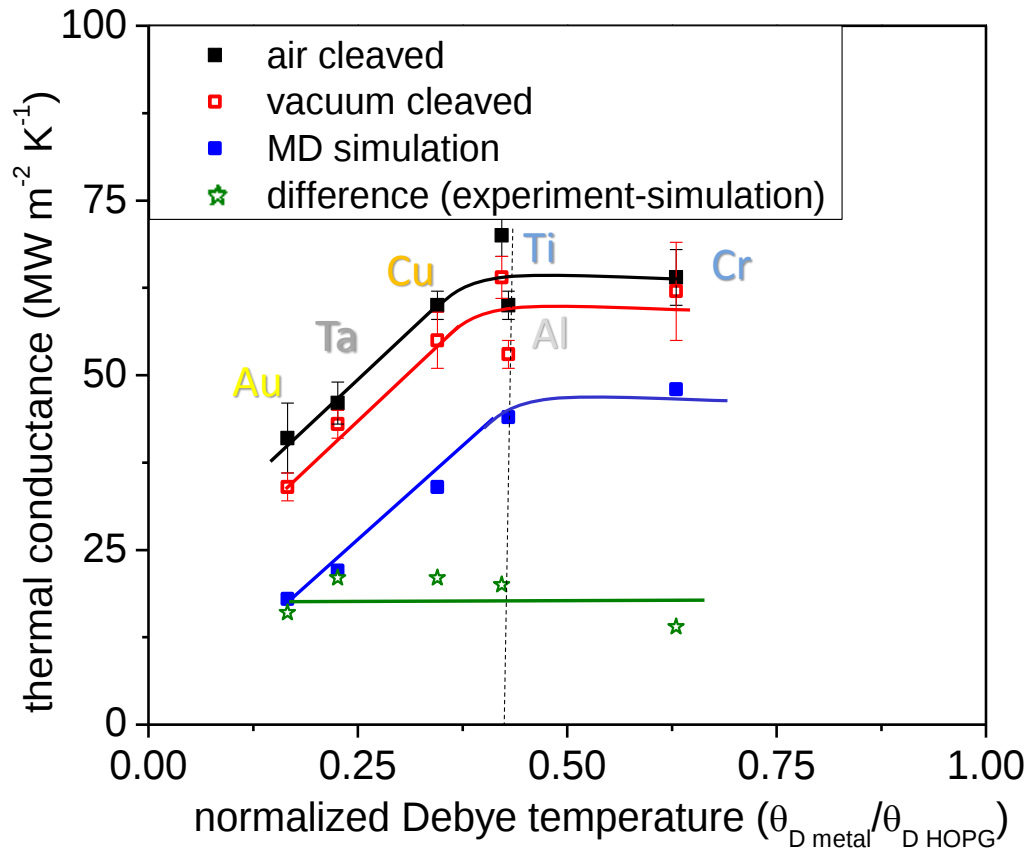
$$G = \int_{\omega} k_B \chi(\omega) \Phi_1(\omega) \Phi_2(\omega) d\omega$$



- Conductance scales with Debye temperature of the metal (diffuse mismatch model works well)
- The constant is good approximation for spectral interfacial conductance for all studied metal-carbon interfaces



Interface Conductance for HOPG and Different Metals



Observations:

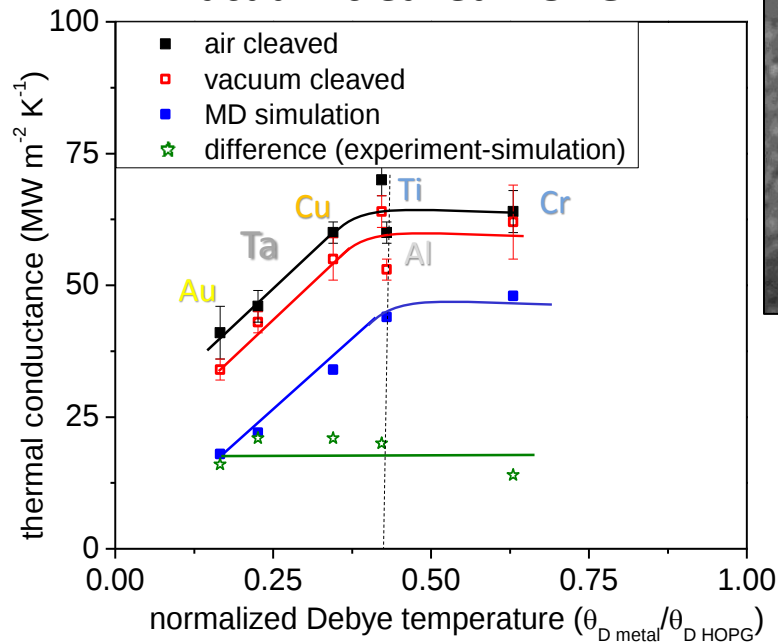
- Strong dependence on metal for $\theta_{D \text{ metal}} < 400\text{K}$ (~3x)
- Conductance levels off above ~0.5 ($\theta_{D \text{ metal}} \sim 400\text{ K}$)
- Conductance for vacuum cleaved HOPG less than air cleaved (within error bars, but repeatable)



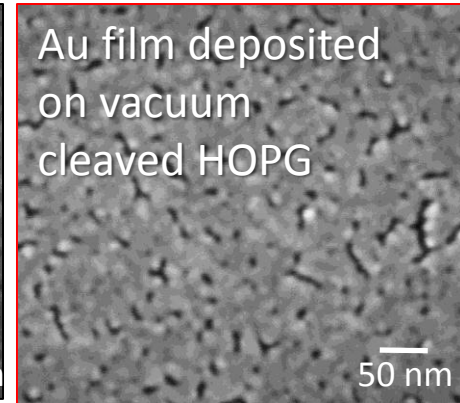
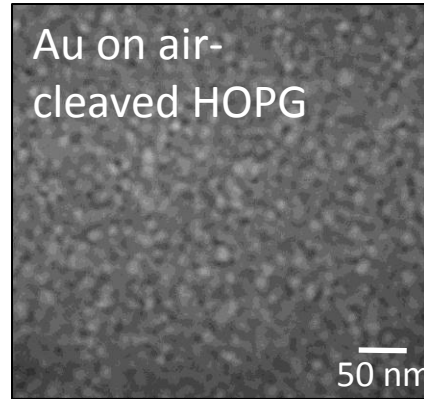
Effects of Vacuum Cleaving on Metal Morphology



≈15% reduction in G for vacuum cleaved HOPG



Lagally, et al. Nature, 417 (2002) 902



>15% reduction in interfacial contact area

Same phenomena drives growth of ice dendrites on clean glass

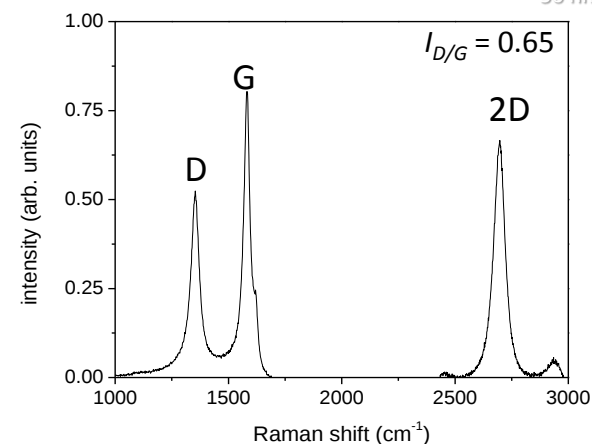
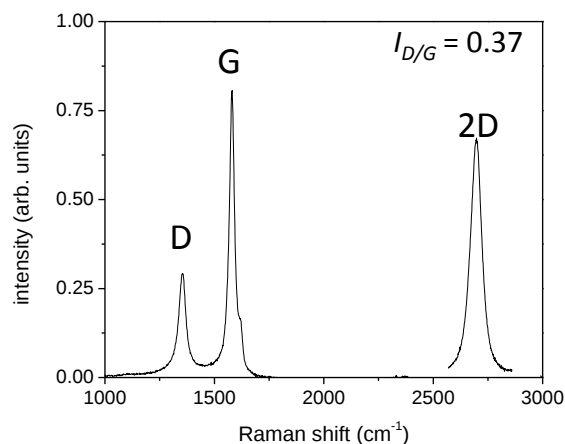
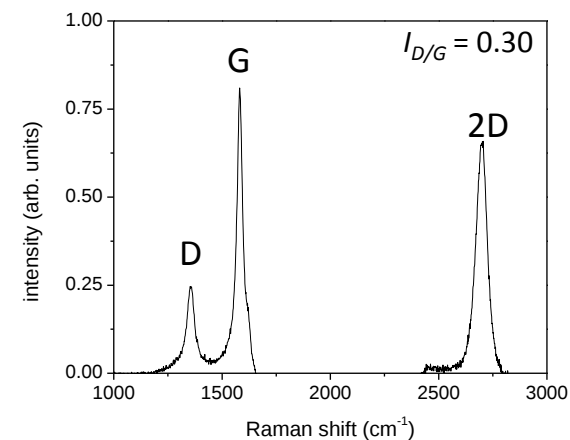
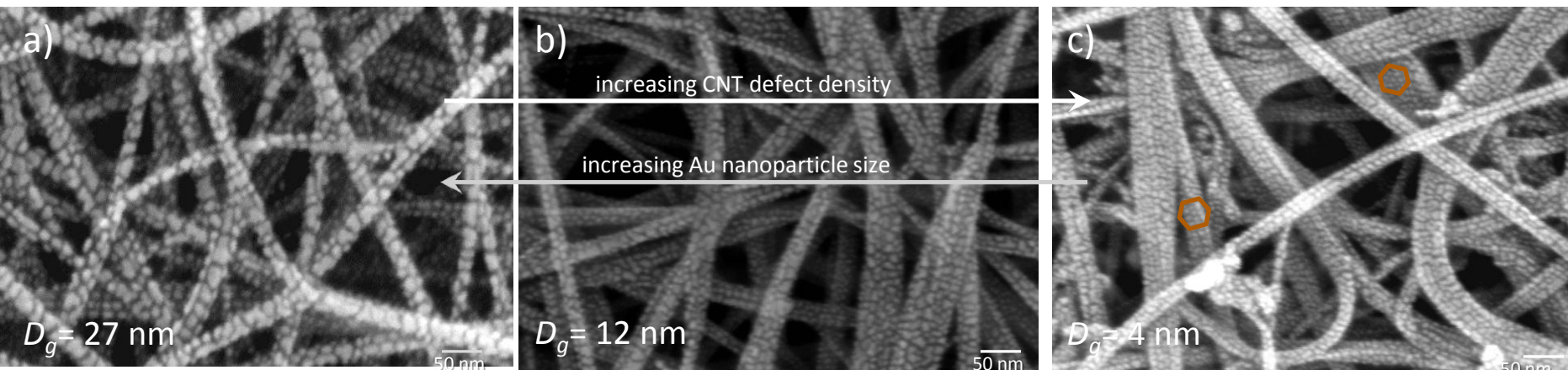


step barrier

island corner barrier

Higher metal diffusivity on clean HOPG than on metal aggregates due to ES barriers

Controlling Particle Size by Introducing Defects *in-situ*



Consider nucleation kinetics

$$\Delta G(j) = -j\Delta\mu + j^{2/3}X \quad \text{where,}$$

$$X = \sum_k C_k \gamma_k + C_{AB}(\gamma^* - \gamma_B)$$

γ^* = interface energy
 γ_B substrate surface energy
 C_k constant describing surface area island face
 C_{AB} constant describing surface area film/substate

Differentiate ΔG to find critical size (at maximum)

$$i = \left(\frac{2X}{3\Delta\mu} \right)^3$$

Decreasing X by introducing defects
decreases critical cluster size



targeting multifunctionality in carbon fibers



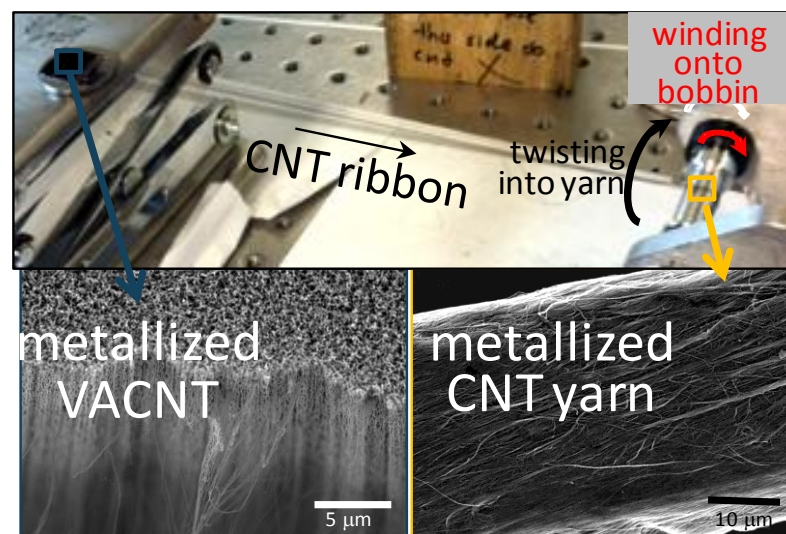
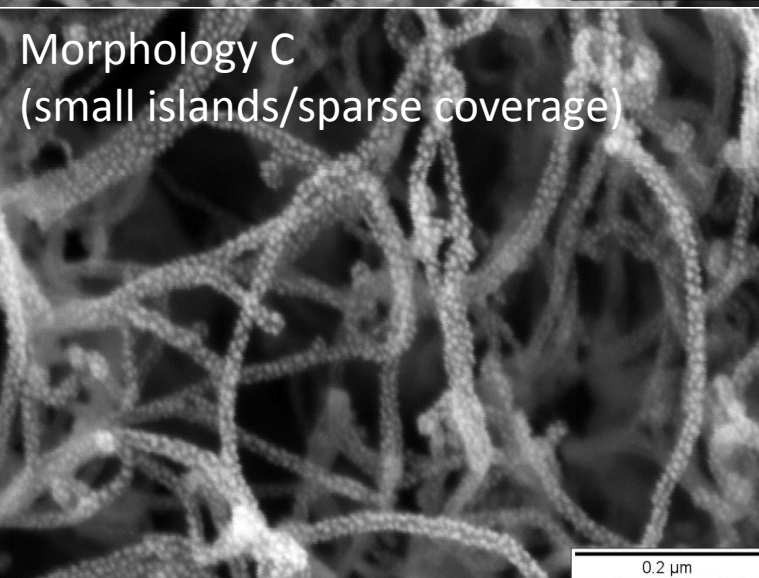
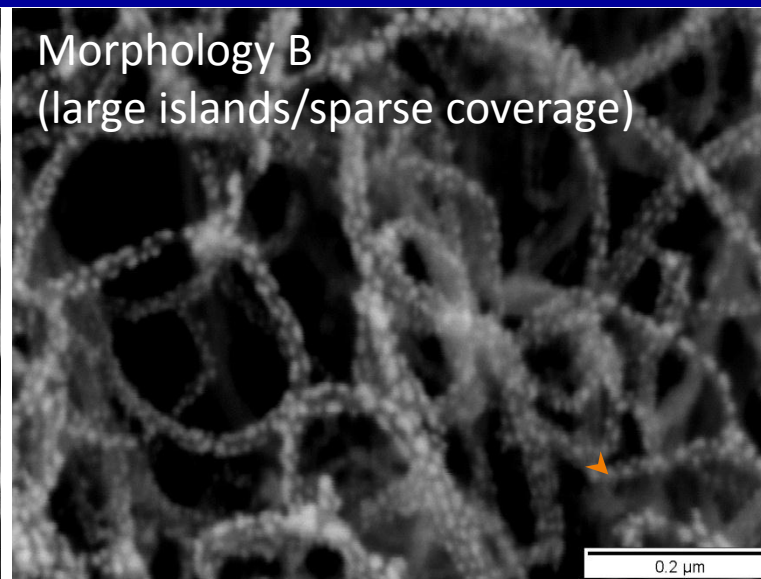
	Tensile strength	Thermal conductivity	Electrical conductivity
Carbon fiber (IM8)	6.1 Gpa	500 W m ⁻¹ K ⁻¹ at 22 °C	1 x 10 ³ S cm ⁻¹ at 22 °C
CNT yarn SOTA	3.5 GPa	60 W m ⁻¹ K ⁻¹ at 22 °C	2 x 10 ⁴ S cm ⁻¹ at 22 °C
Proposed target	10 GPa	500 W m ⁻¹ K ⁻¹ at 22 °C	4 x 10 ⁴ S cm ⁻¹ at 22 °C
Individual SWCNT	100GPa	3000 W m ⁻¹ K ⁻¹ at 22 °C	7 x 10 ⁴ S cm ⁻¹ at 22 °C

Copper σ —6 x 10⁵ S cm⁻¹

CNT yarn demonstrates comparable properties to state of the art carbon fibers, however, is still far away from single nanotube values

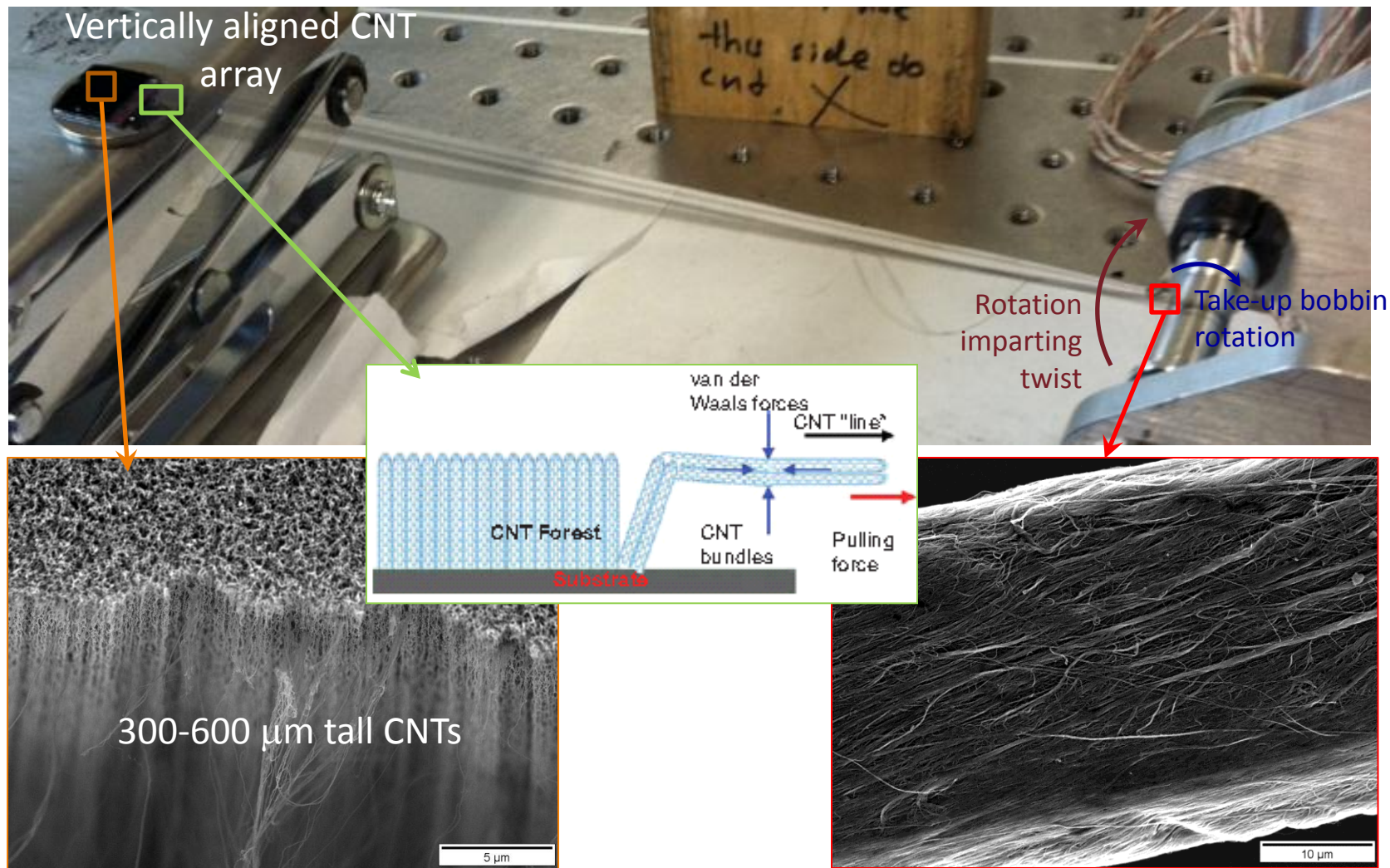


Investigating Effects of Morphology on CNT Yarn Properties





Dry Spinning of CNT Arrays into Carbon Nanotube Fibers





Correlation between particle size and melting point in literature



- **The relationship between the melting point of bulk material and a particle is given by,**

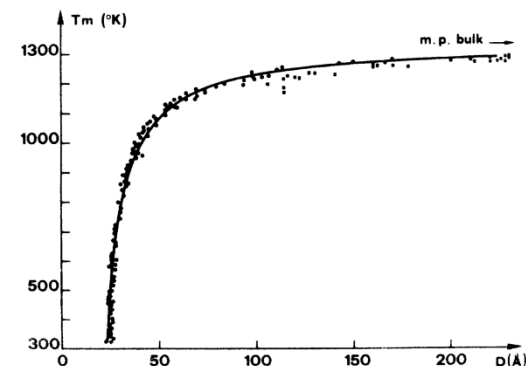
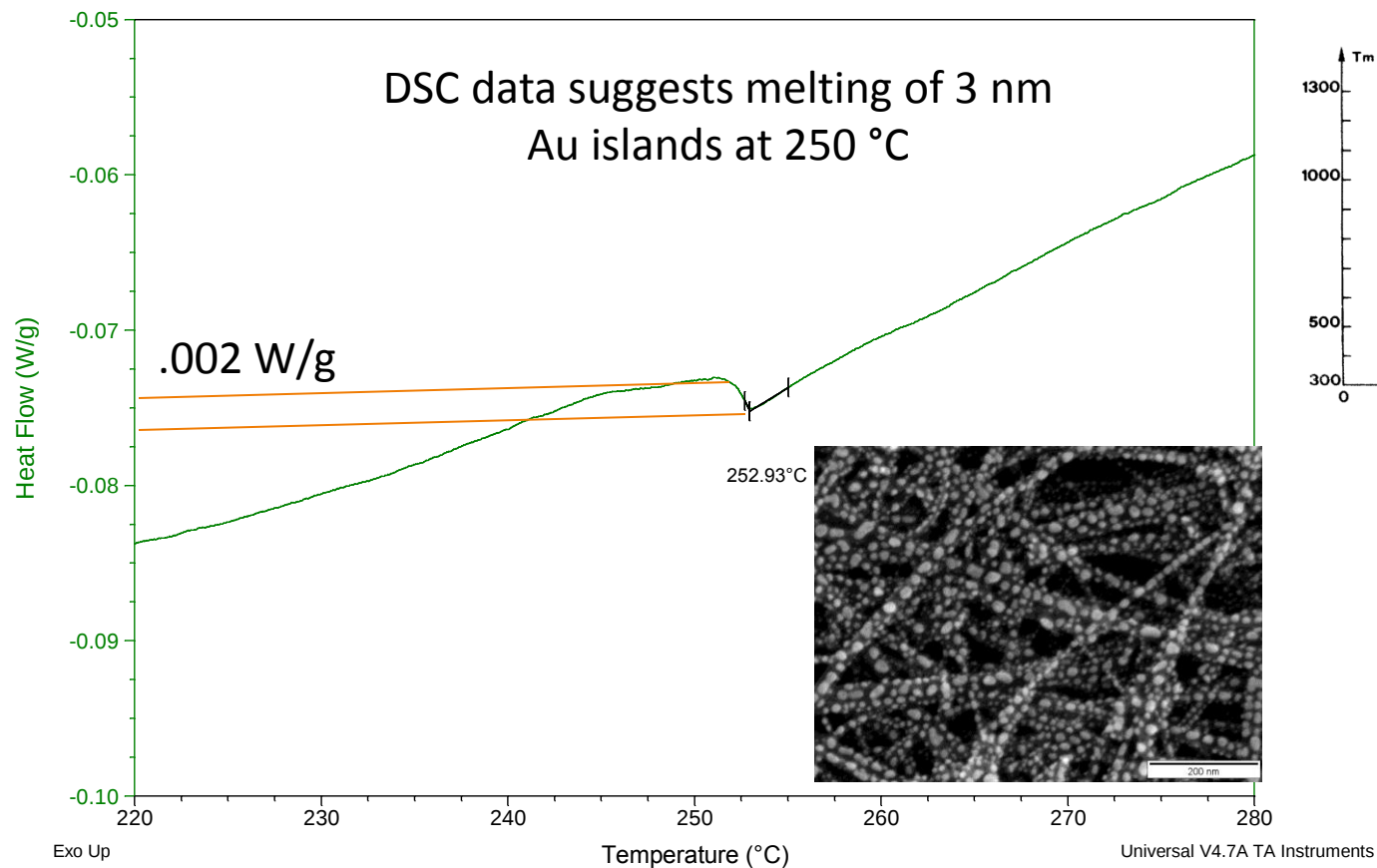
$$T_b - T_m = \left[\frac{2T_b}{\Delta H \rho_s r} \right] \left[\gamma_s - \gamma_l \left(\frac{\rho_s}{\rho_l} \right)^{2/3} \right] \star$$

where, T_b = melting point of bulk material, T_m = melting point of particle, r = radius of particle, ΔH = molar latent heat of fusion, γ and ρ = surface energy and density.

****Buffat P, Borel JP (1976) Size effect on the melting temperature of gold particles. Physical Review A 13 (6):2287-2298***

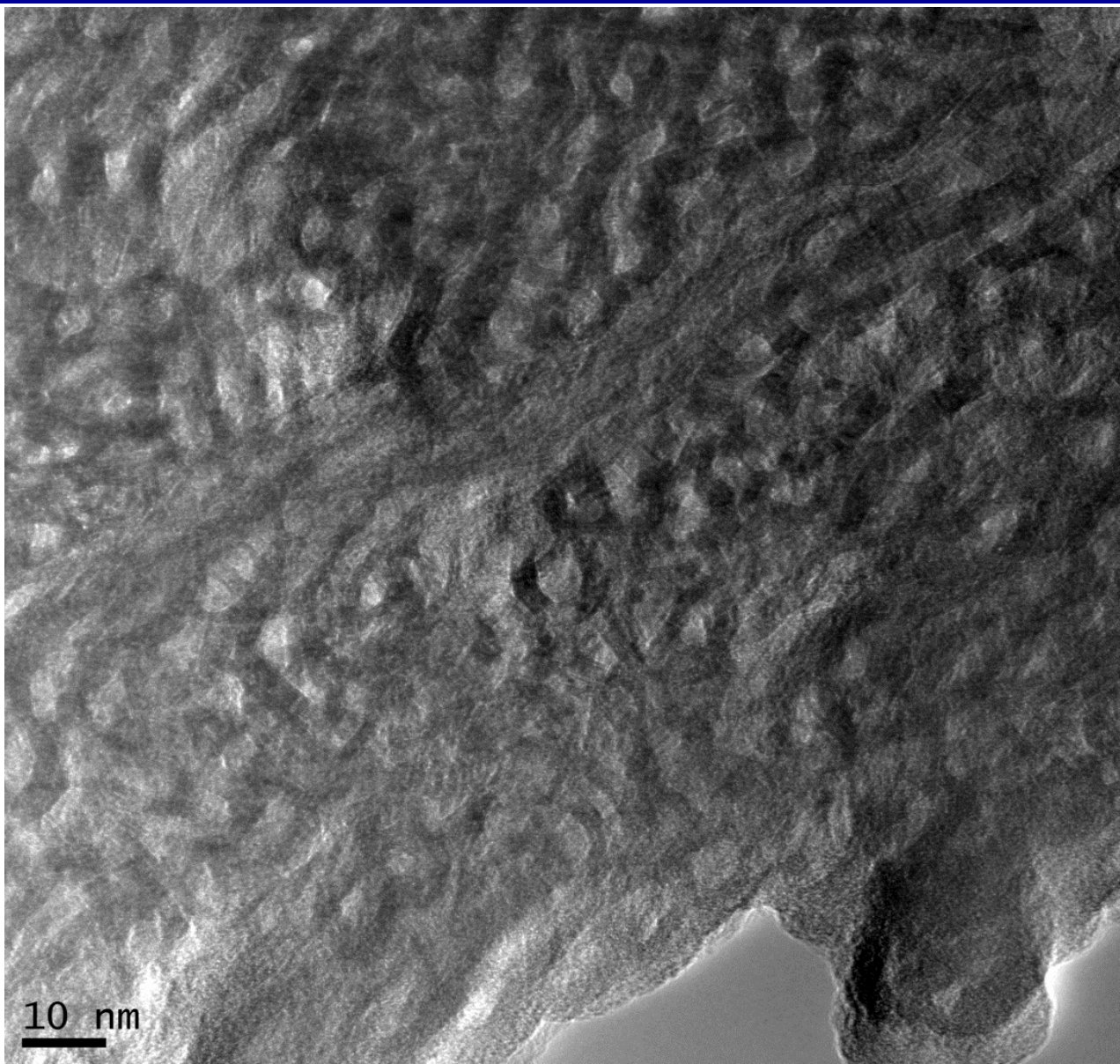


Particles with Tailorable Melting Points





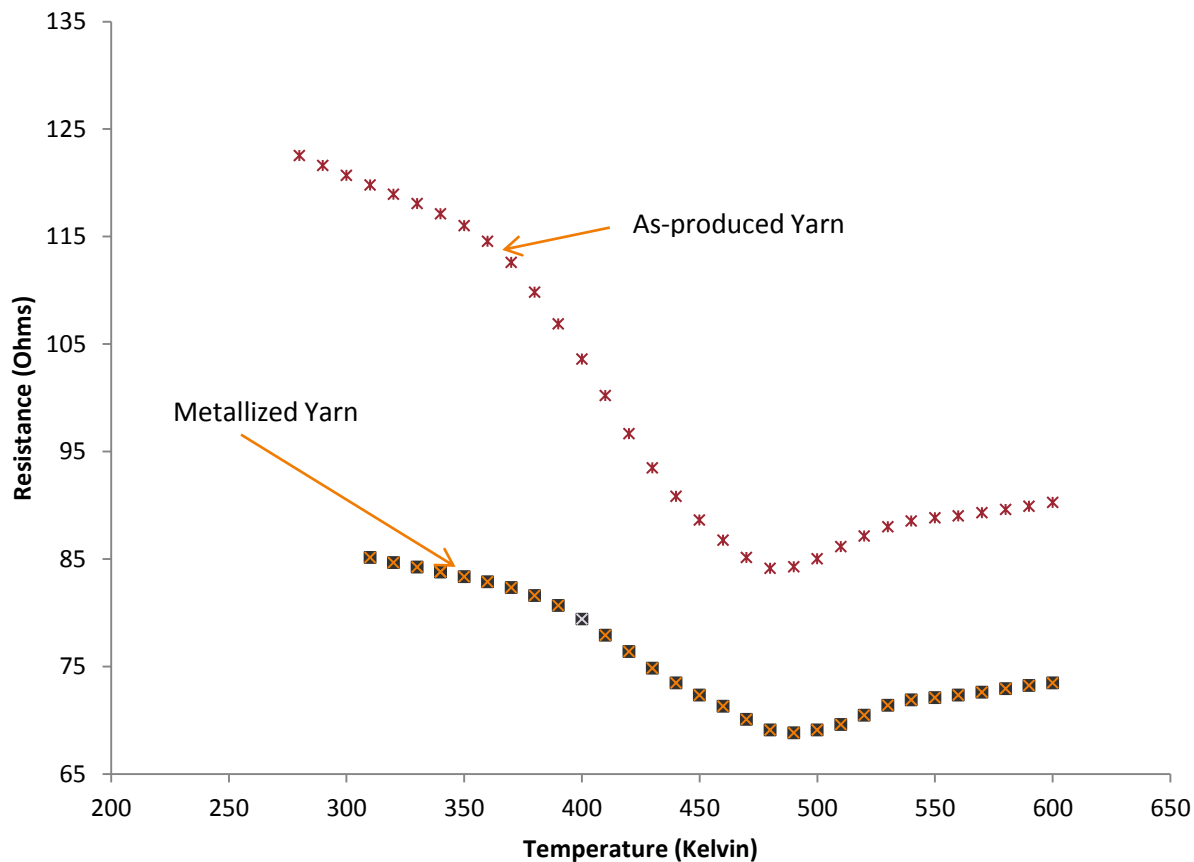
High Resolution TEM Micrographs of NT Yarn Cross-section



10 nm



Electrical Properties of CNT Yarn by 4 Wire Probe



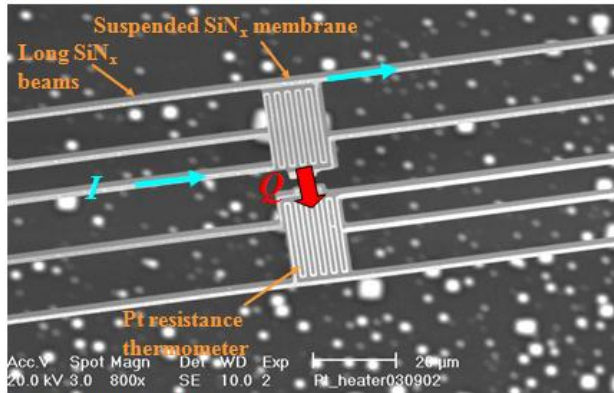


Microscale Thermo-Mechanical Measurements



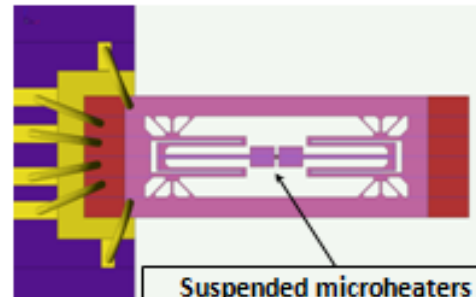
Thermal Measurements of Nanotubes and Nanowires

Thermal conductance: $G = Q / (T_h - T_c)$

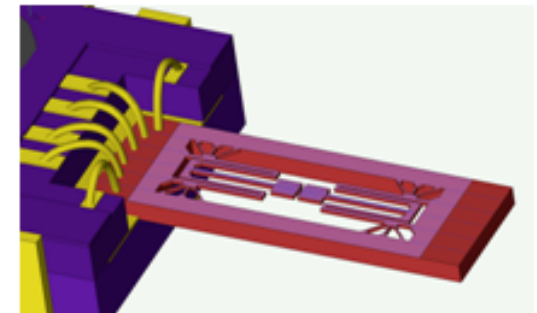


Kim et al, *PRL* **87**, 215502
Shi et al, *JHT*, in press

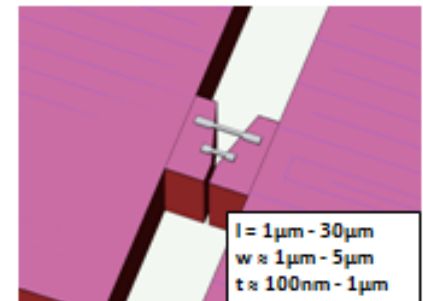
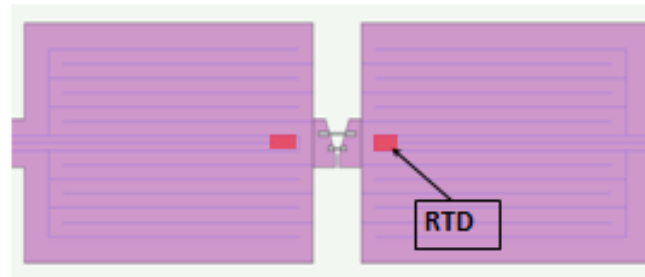
In-Situ Thermal Conductivity Experiment using AFRL/MCF Device



Suspended microheaters with embedded RTDs

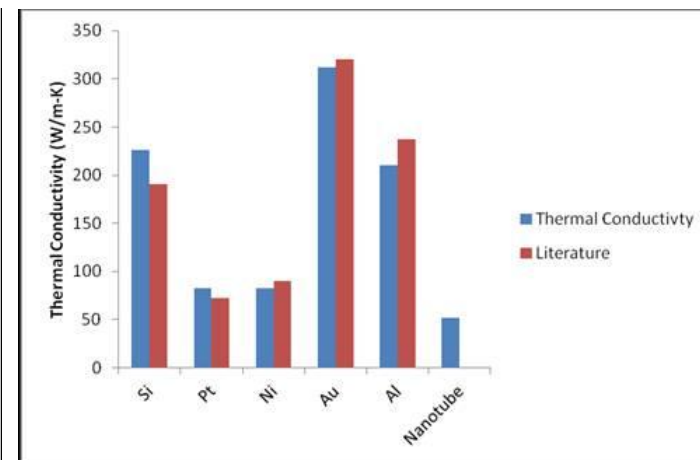
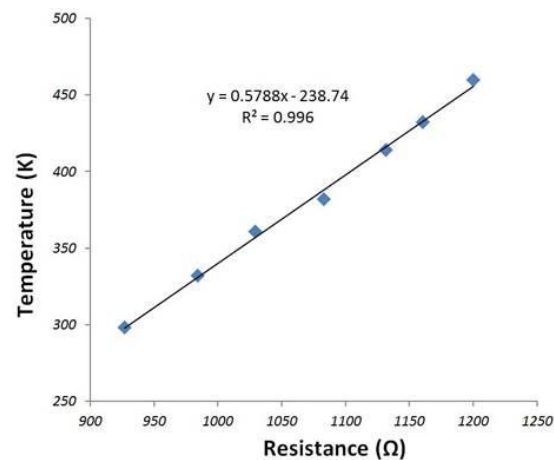
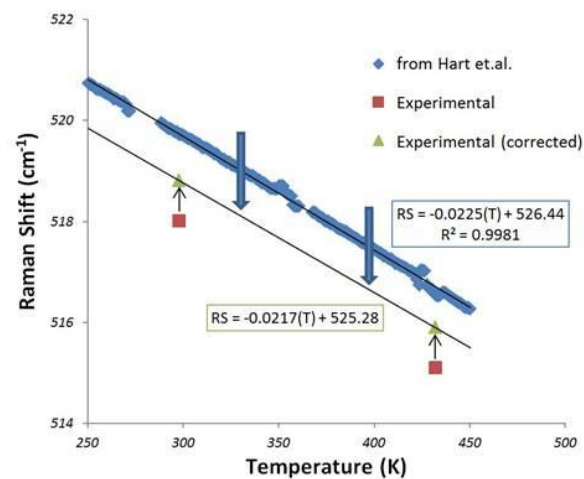
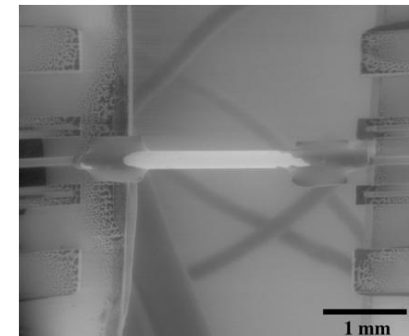
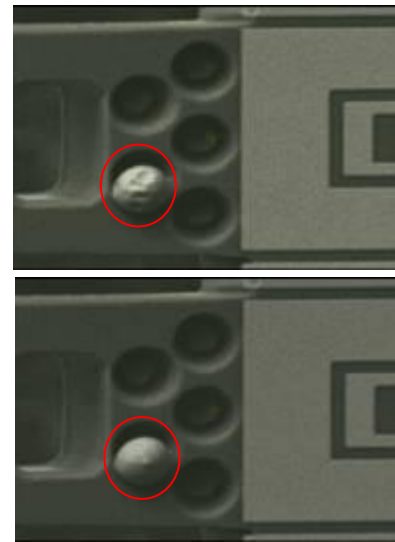
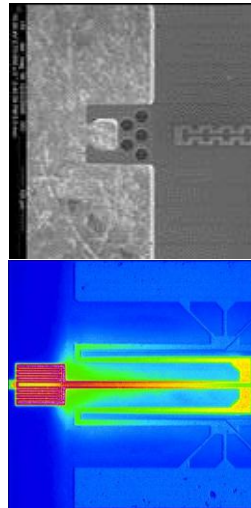
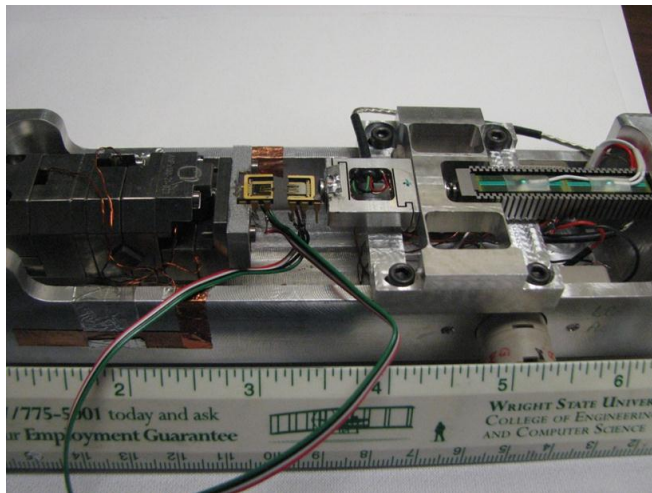


Microsamples



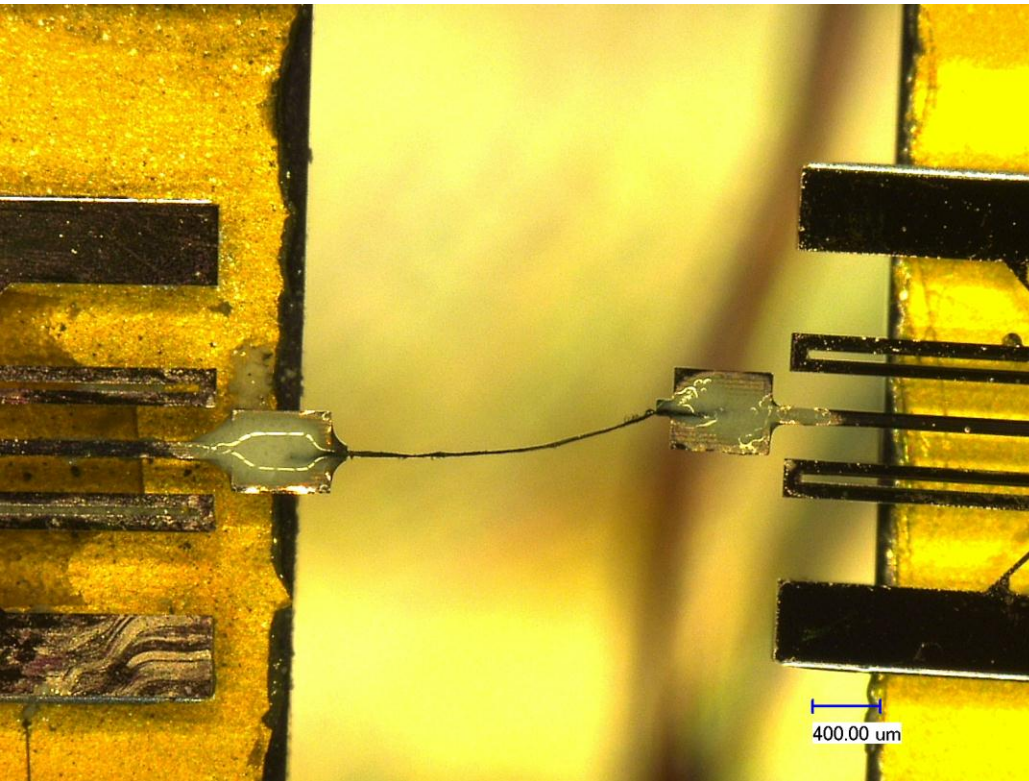


Temperature Calibration of the System & K Measurement of Standard Metal Wires





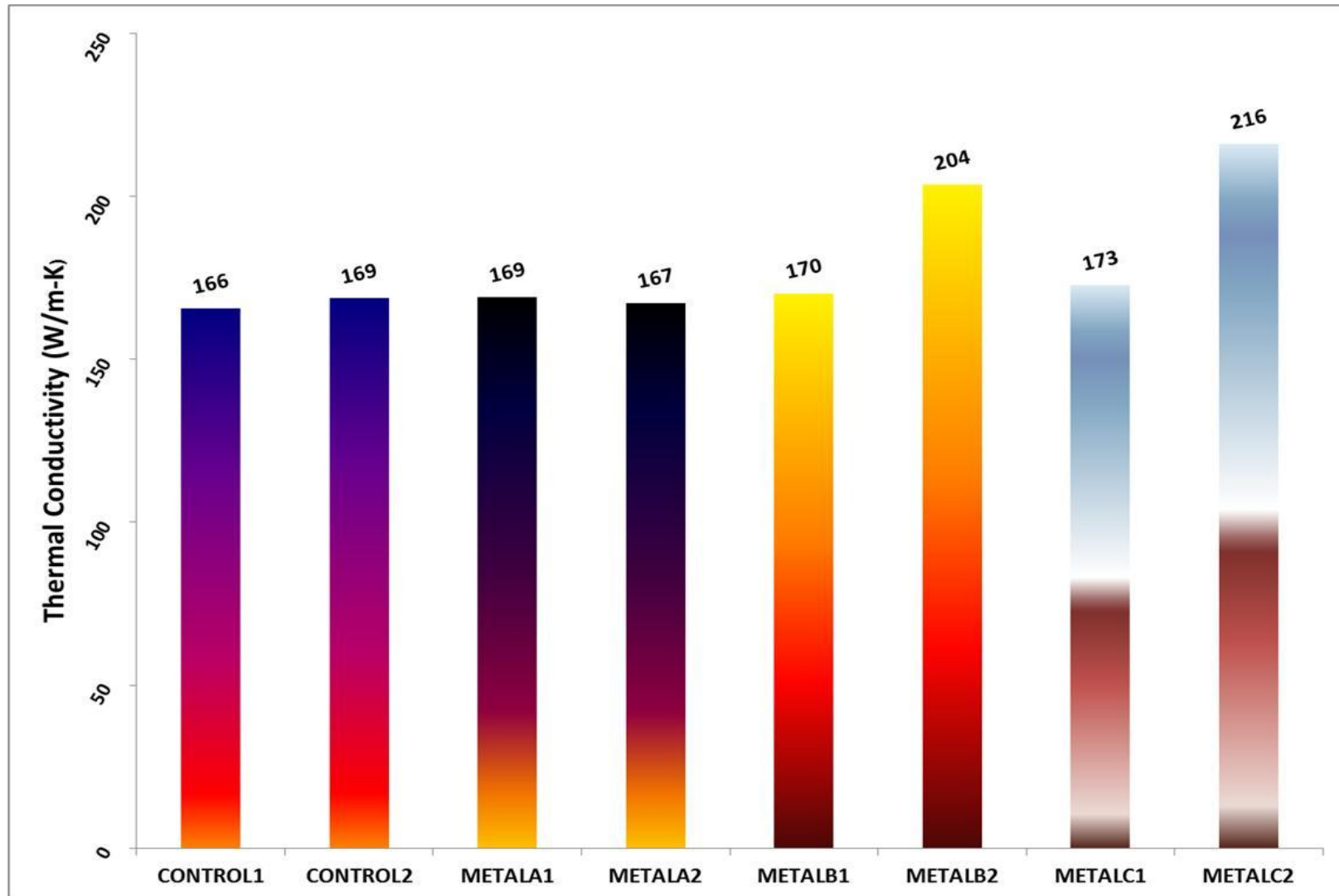
Thermal Conductivity Measurement Testing Protocol



- k for each sample measured 3 times
 - First at RT
 - Annealed at 300 °C & cooled to RT
 - Repeat measurement at RT
- Omega® thermal grease used at the interface
- All measurements performed in a vacuum chamber
- Length and cross sectional area measured by EM

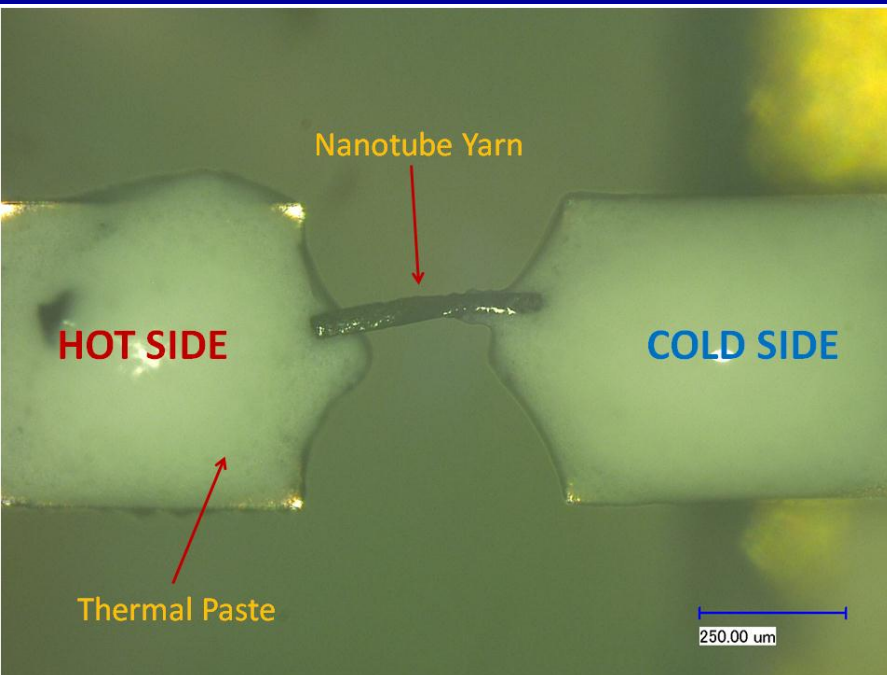


Measured Thermal Conductivity

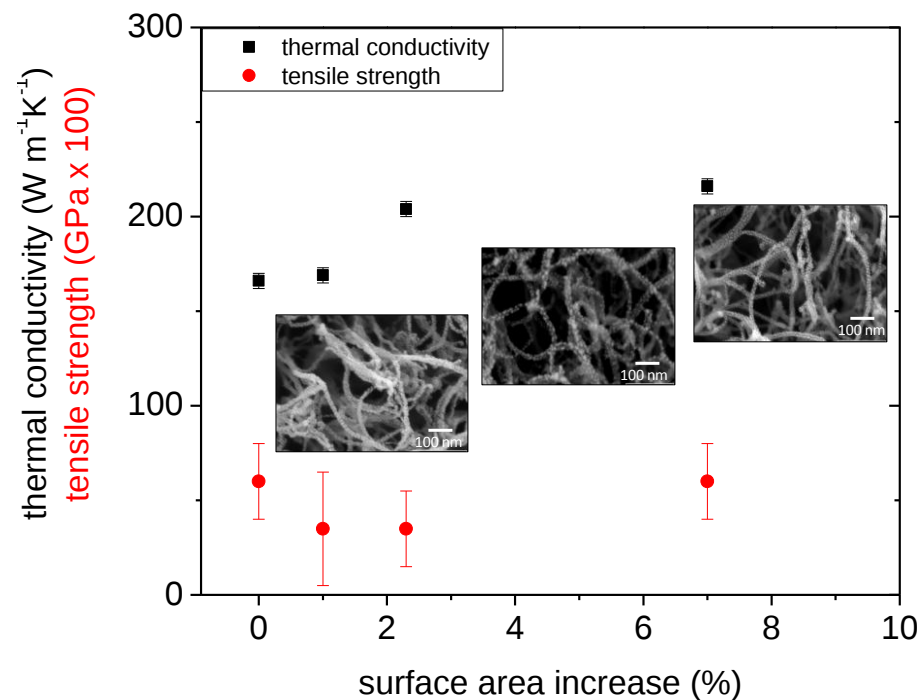




Micro-scale thermal conductivity and mechanical property measurements



Metallization and annealing result in 30% increase in thermal conductivity without compromising mechanical strength

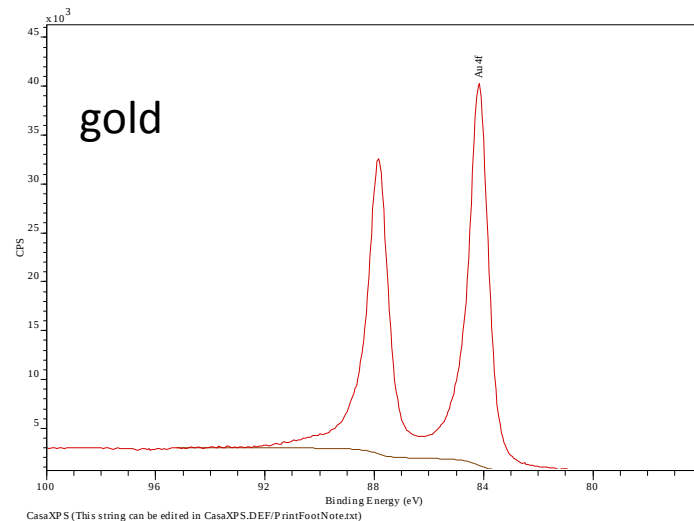
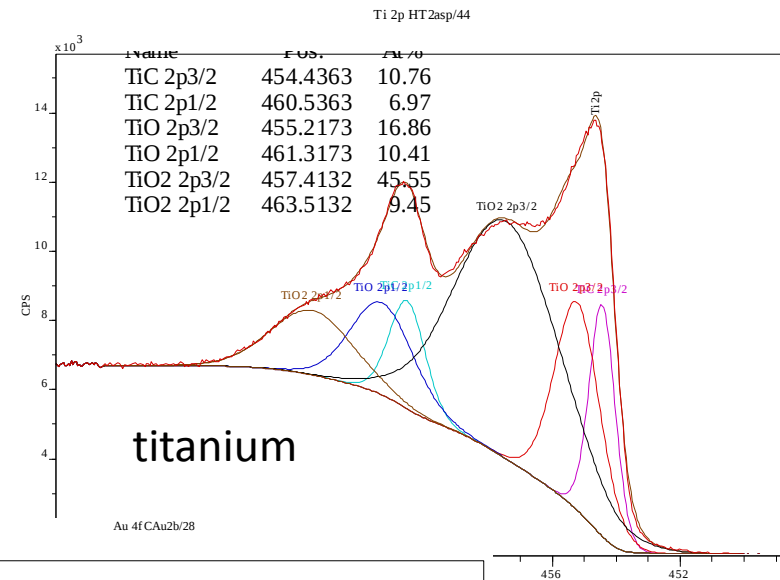
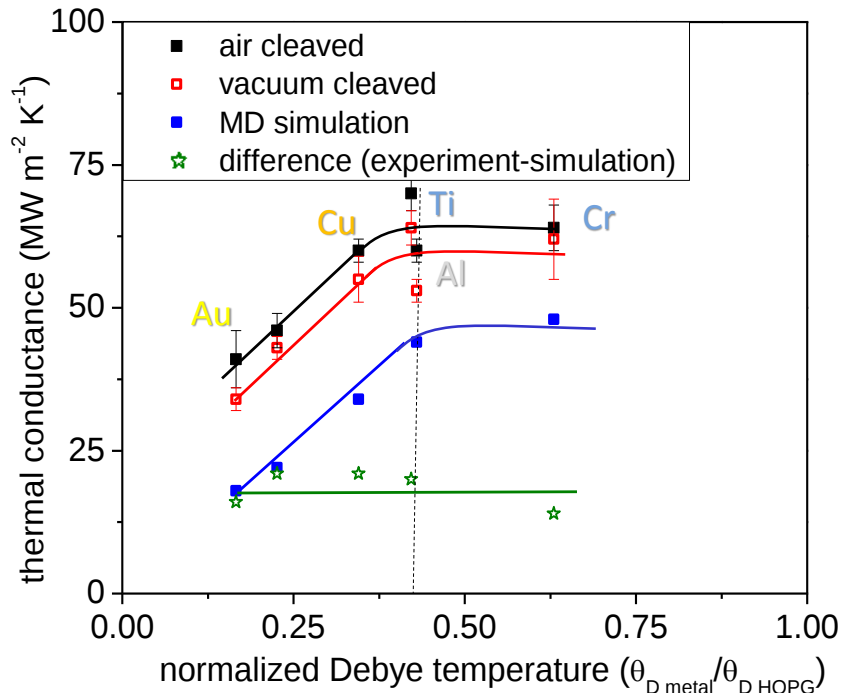




Materials Selection: Intrinsic vs. Extrinsic Effects on Conductance



Gold has lowest intrinsic conductance, however highest oxidation resistance

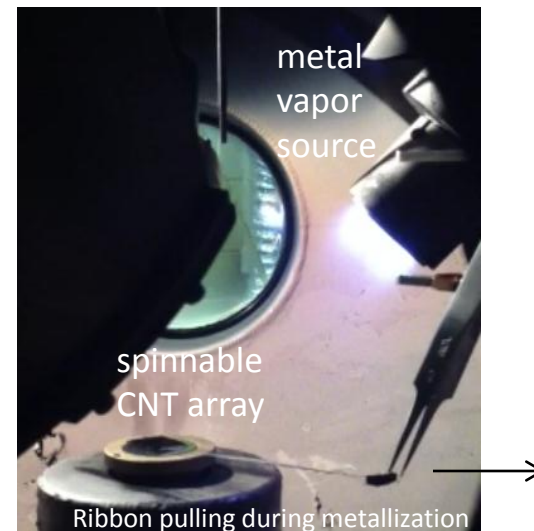




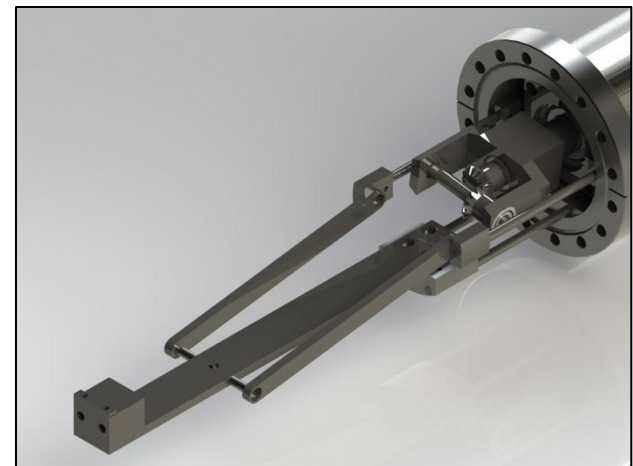
Overcoming Difficulties with non-gold Metallization within Vacuo Spinning



metallizing while spinning

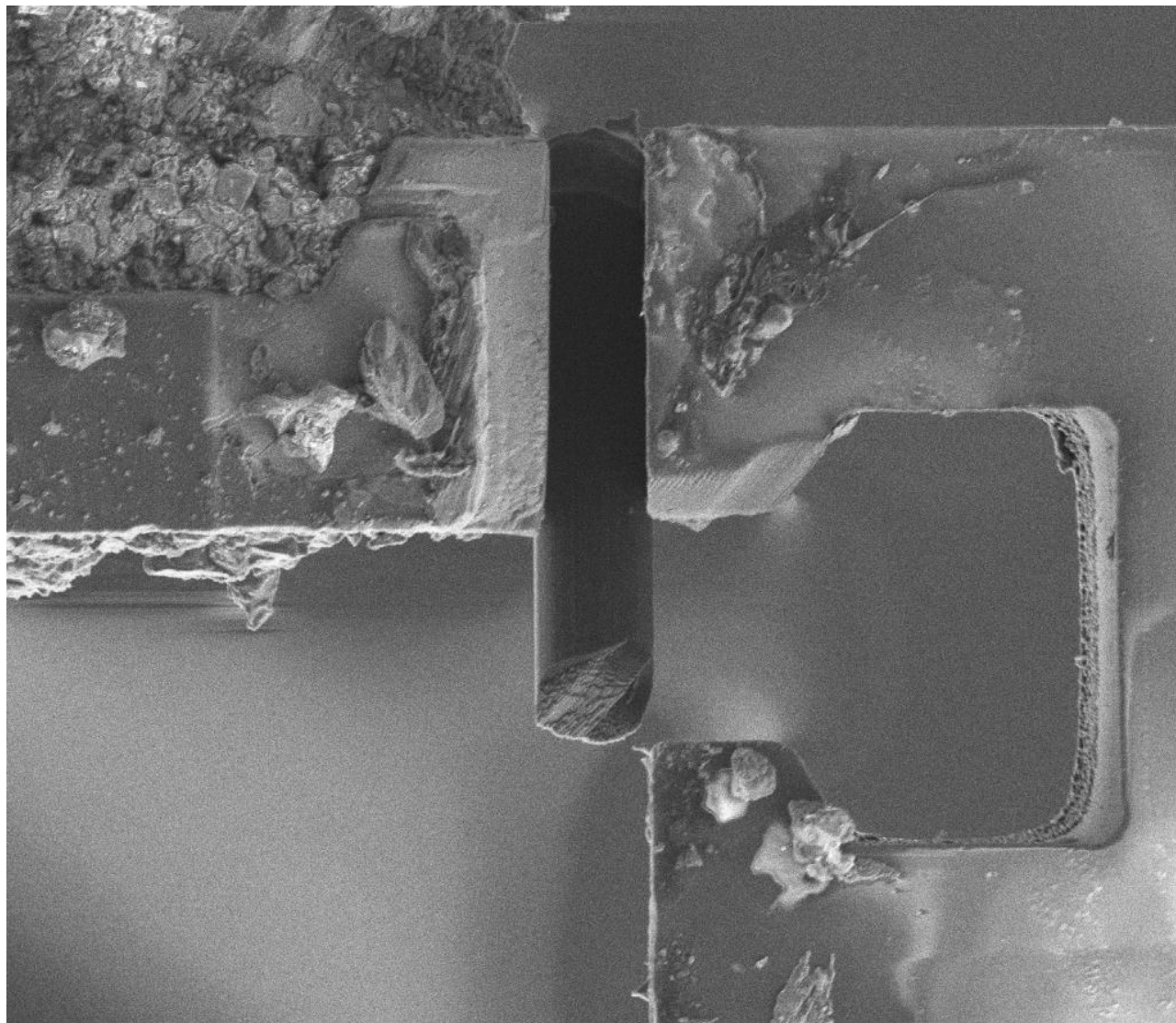


**in situ spinning and
annealing during
UHV metallization to
avoid oxidation at
critical interfaces
affecting transport**





Direct Concurrent Thermal and Mechanical Property Measurement of Single Carbon Fiber

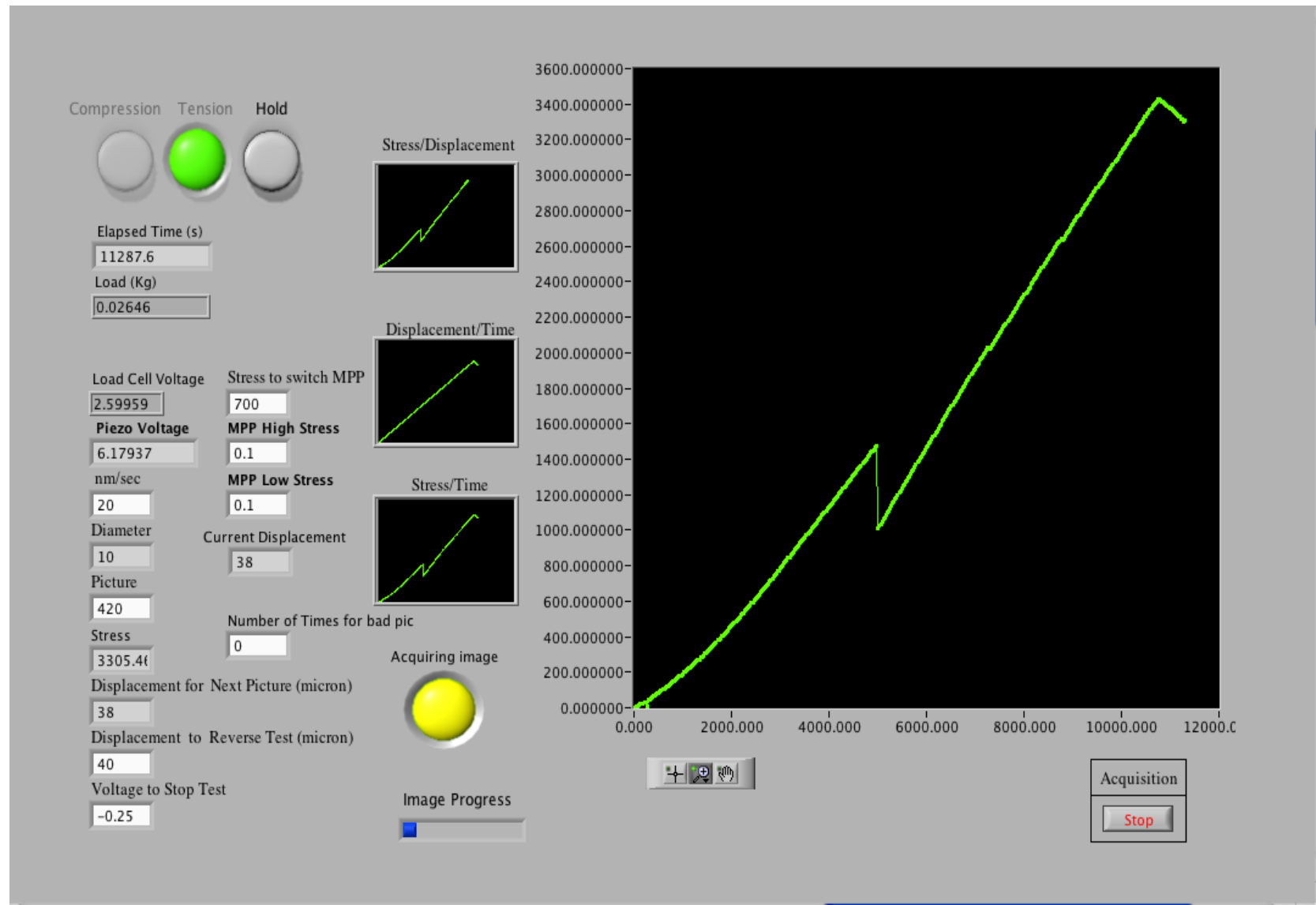


E-Beam	Mag	Det	Spot	FWD	Tilt	Scan	20 μ m	
5.00 kV	2.50 kX	SED	4	5.000	0.0°	H 6.34 s		



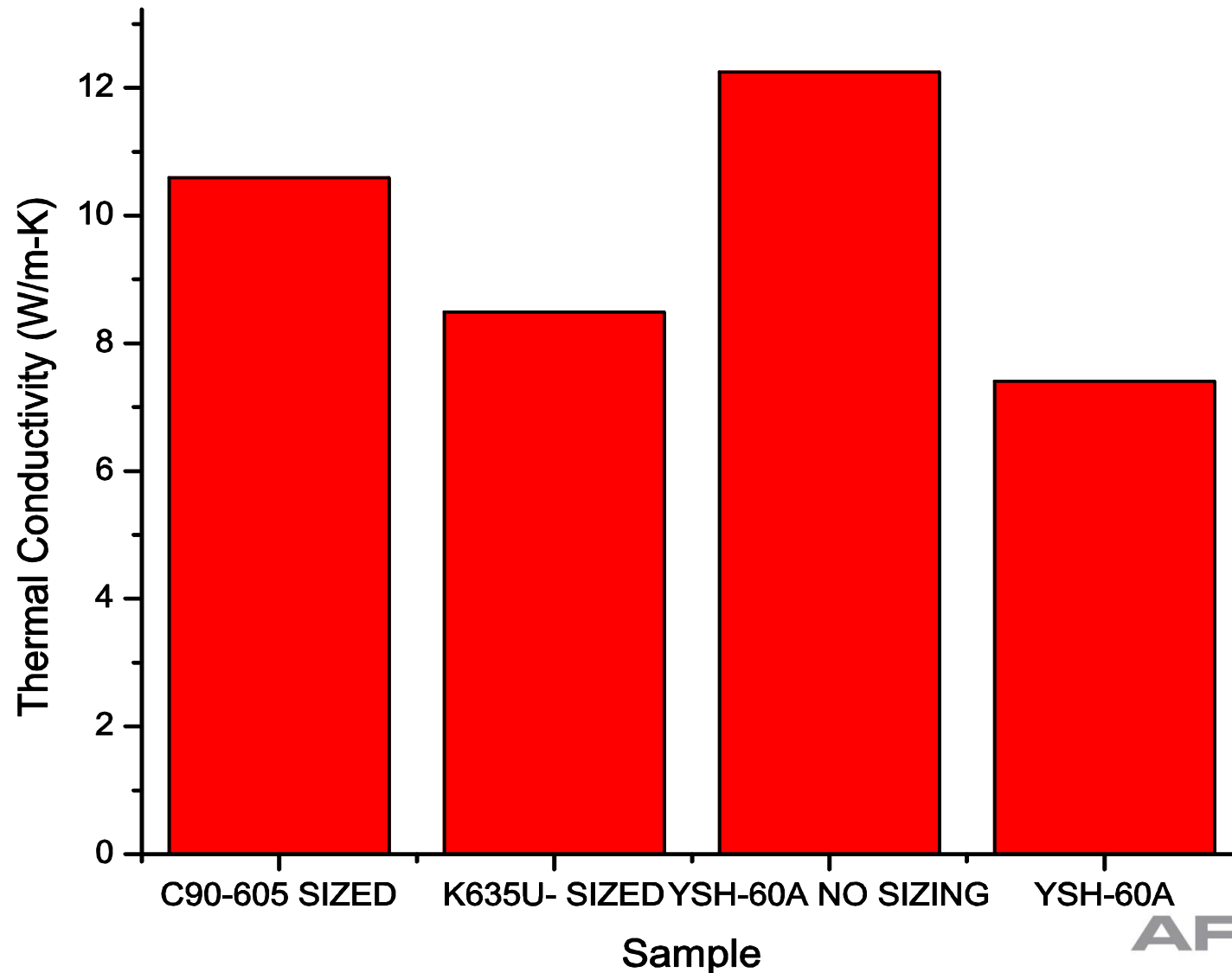


Load Displacement Measurement of Single Carbon Fiber Diameter $\sim 12 \mu\text{m}$





Transverse Thermal Conductivity of Pitch Carbon Fibers





Summary



- **Metal-CNT interface thermal conductance – two dominant phenomena**
 - Electronic heating
 - Lattice vibration (phonon contribution)
- **Debye temp matching is extremely important for tailoring interface conductance**
- **Submicron scale combined thermo-mechanical property measurement capability**

Nanoelectronic Materials Branch
RXAN Computational Team
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