



Carbon Nanofibers for On-chip Interconnect and Integrated Circuit Applications

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Outline

- Overview
- On-chip interconnects/vias
 - Synthesis
 - DC characterization
- Multi-layer structures
 - IC concepts using multi-layer CNF
- High-resolution microscopy analysis
- CNF-Cu composites for thermal management
- Continuing work



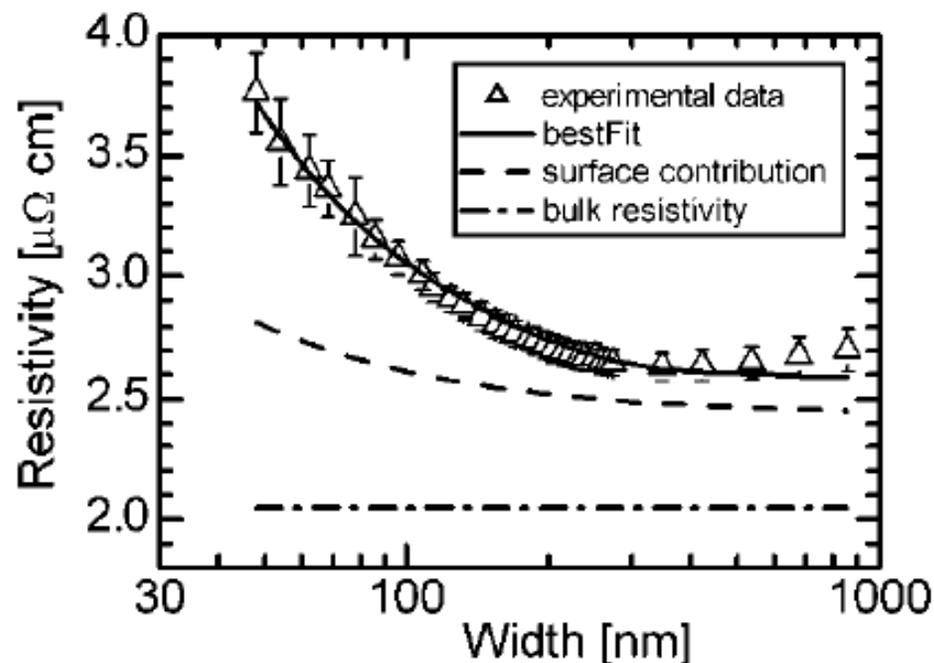
Overview

- On-chip interconnects to replace copper
 - Carbon nanofiber synthesis using PECVD
 - DC measurements of CNF arrays and multi-layer nanofibers
- Microstructural analysis
 - Sample preparation for TEM/STEM imaging
 - Elemental analysis (EDX)
- Thermal Interface Materials (TIMs)
 - Fabrication
 - Thermal resistance characterization



Motivation: Resistivity concerns

- Resistance copper interconnects and vias will soon be reached if scaling trends continue
- CNFs can meet both performance requirements for interconnects in next generation ICs

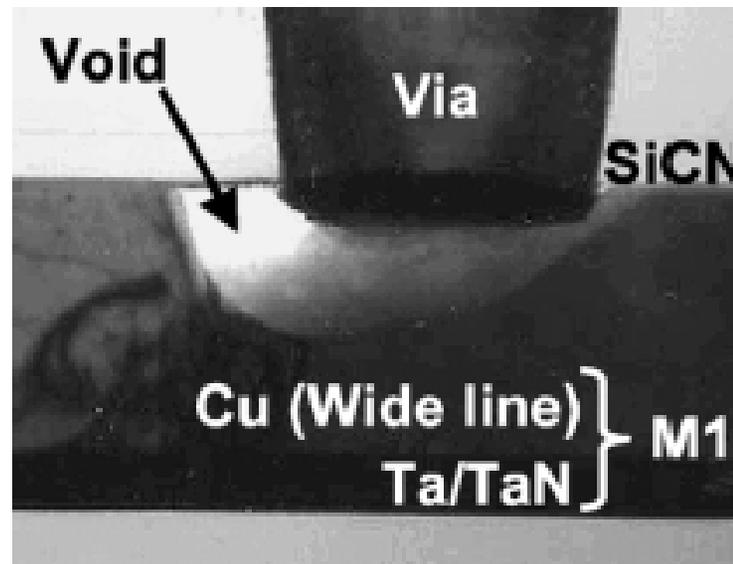


Steinhogel et al., *J. Appl. Phys.* **97**, 023706 (2005)



Motivation: Electromigration

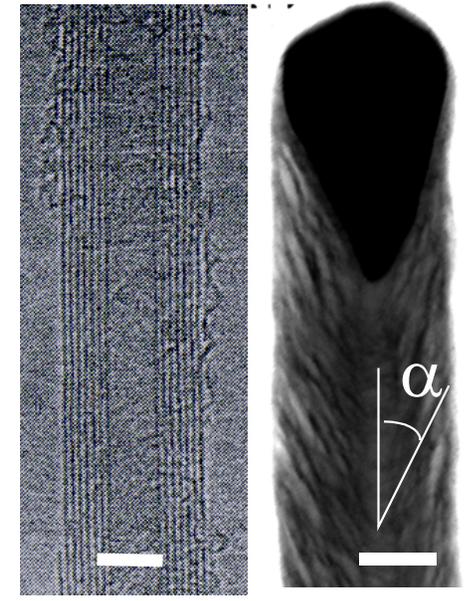
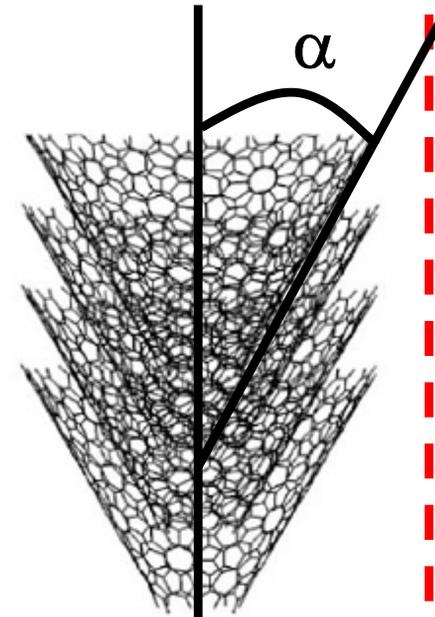
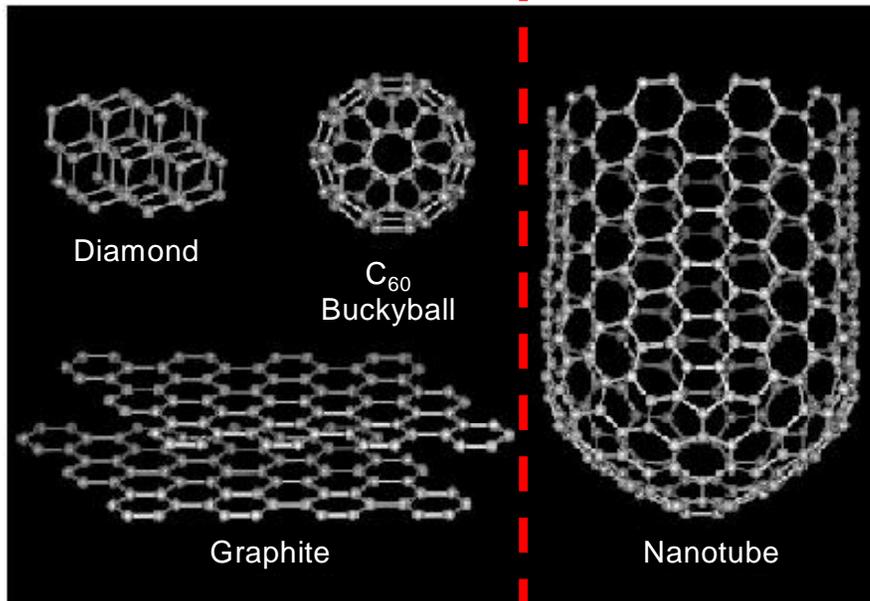
- Electromigration is the failure of an interconnect line or via due to high current stress
- Main source of reliability failures in back-end structures



Saito et al., *IEEE Trans. Elec. Dev.* **51**, 2129 (2004)



Carbon Systems



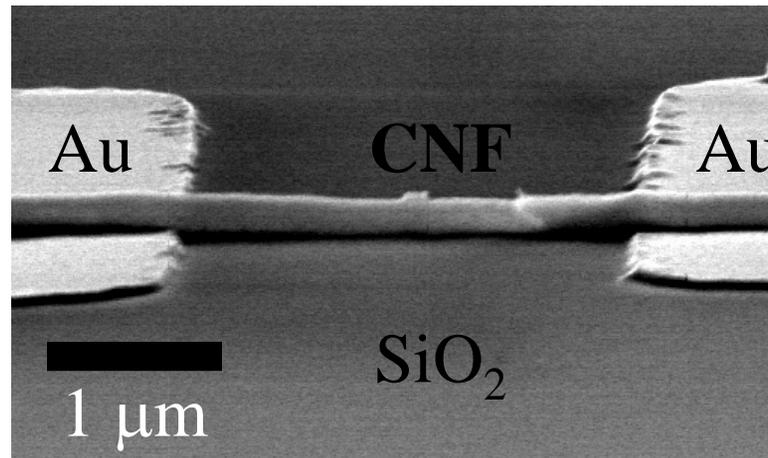
Iijima et al., *Nature*
354, 56 (1991)



CNF Architectures:

Side-contacted geometry

- Contacts are either pre-patterned on the substrate, or deposited after the nanofiber or nanotube has been dispersed onto a substrate
- Contact is made on the sidewall

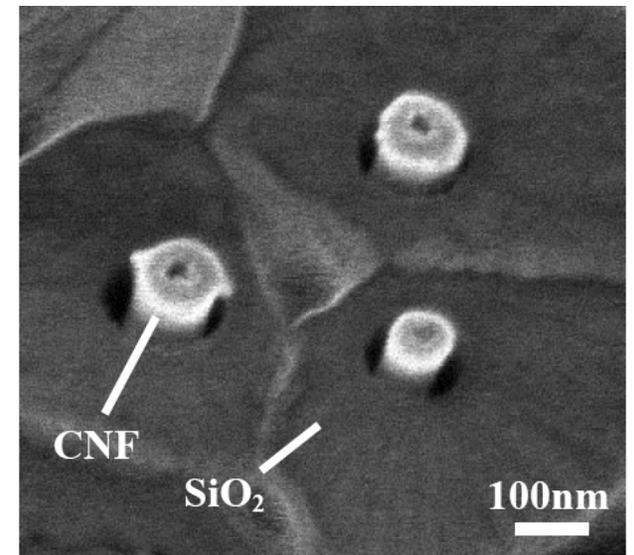
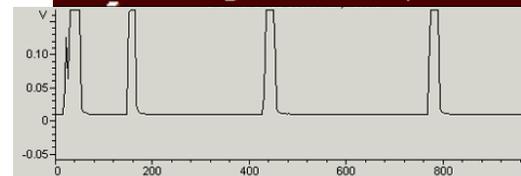
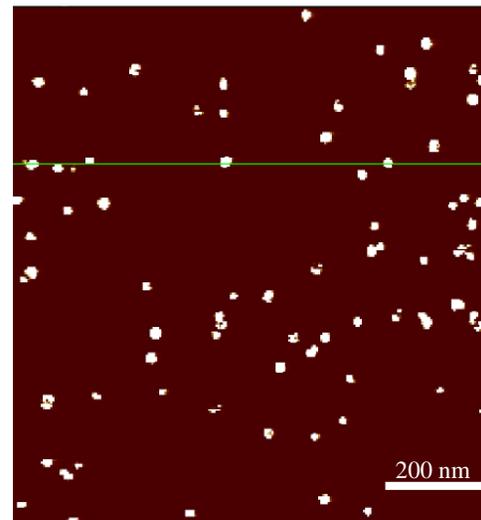
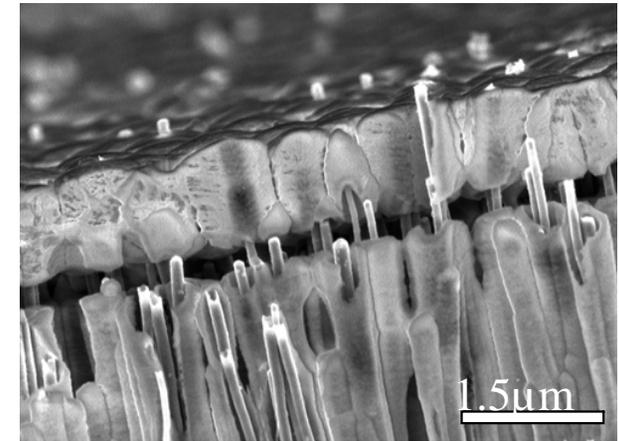
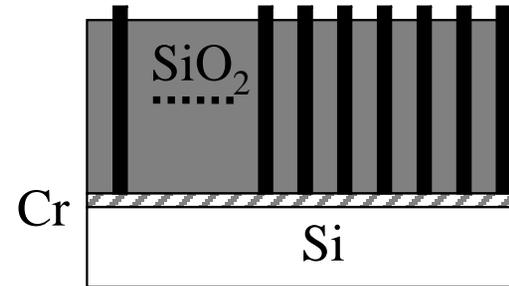




CNF Architectures:

End-contacted geometry

- Nanofibers are grown by plasma-enhanced CVD (PECVD) vertically from a patterned catalyst film
- Contact is made with ends of nanofibers



Current sensing AFM and SEM characterization

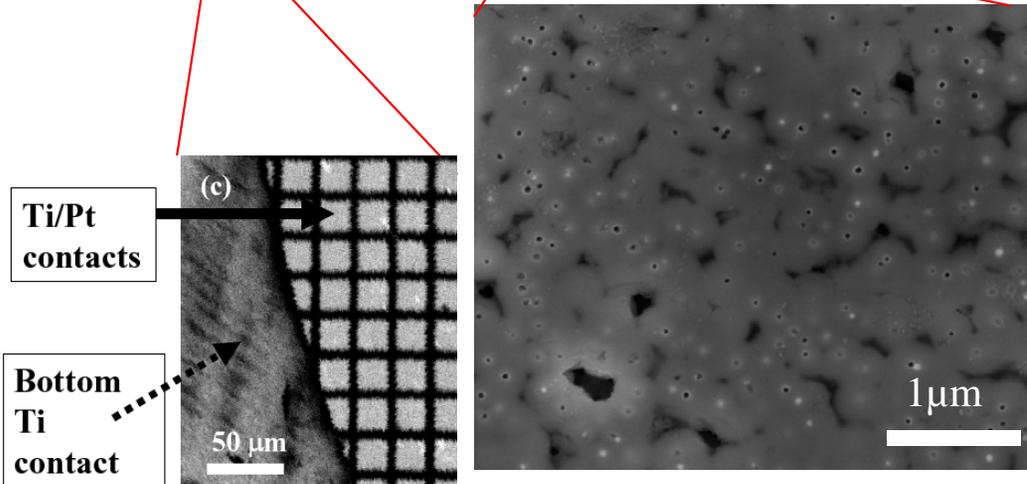
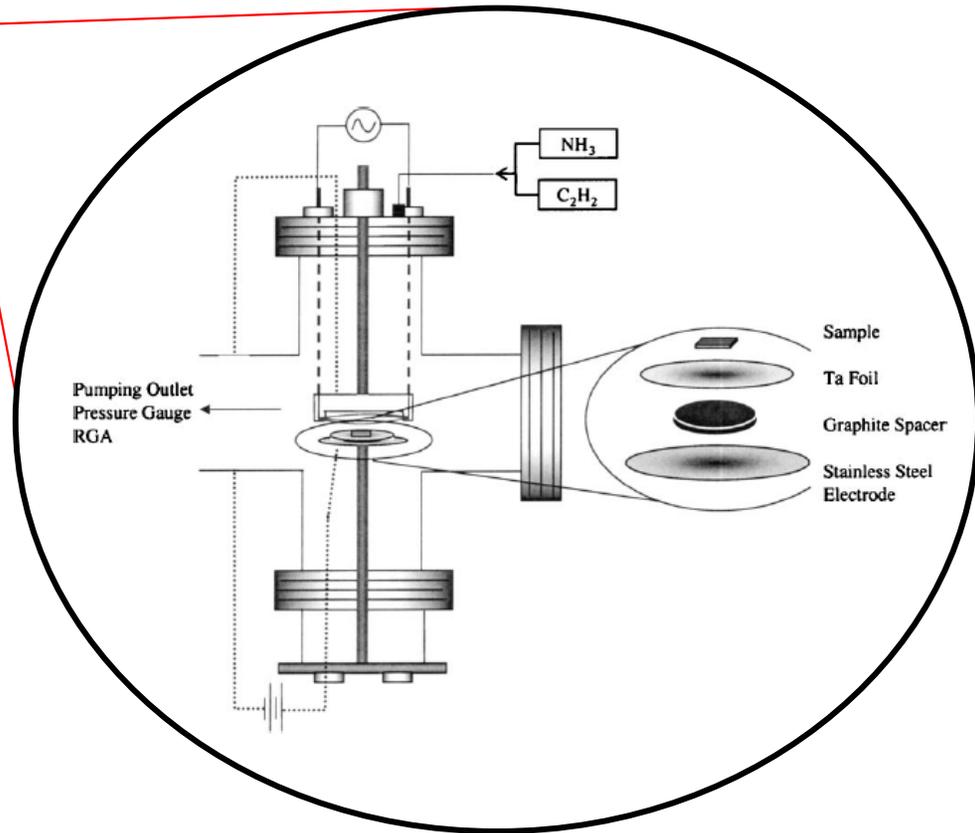
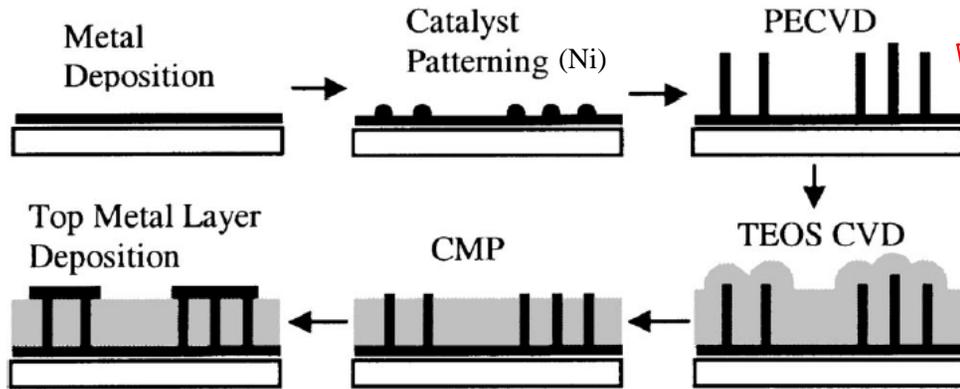
Center for Nanostructures



Process flow for PECVD-grown CNFs

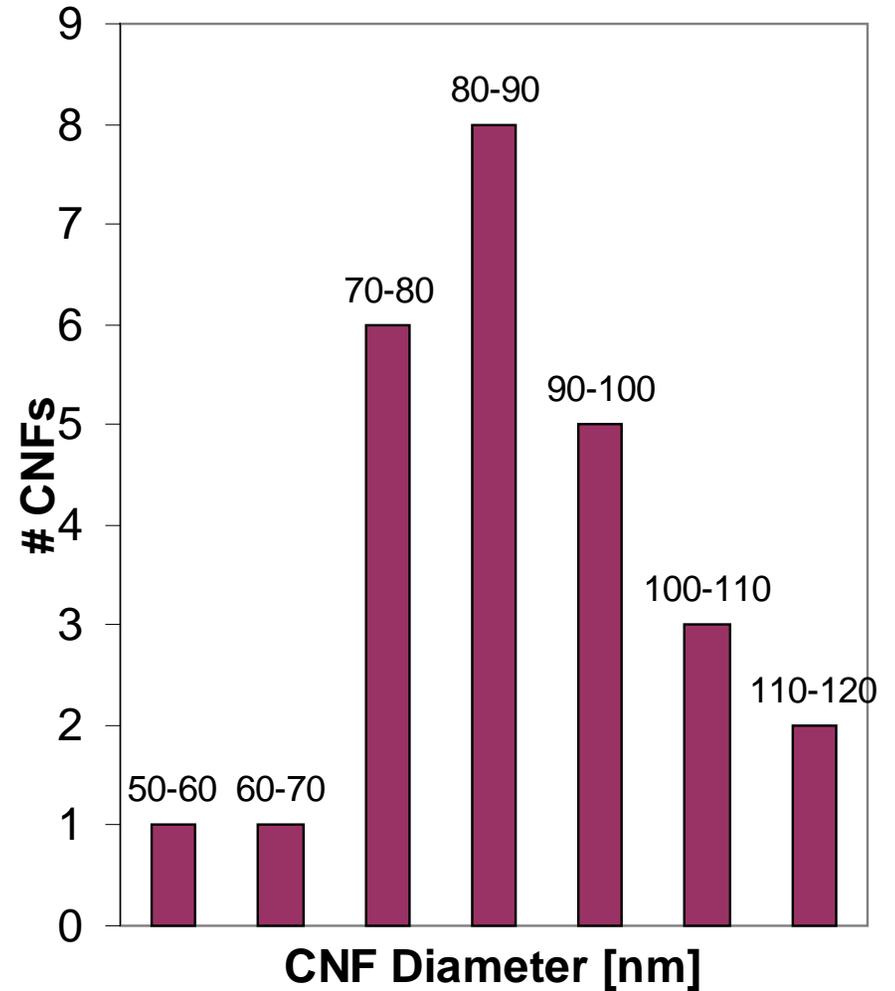
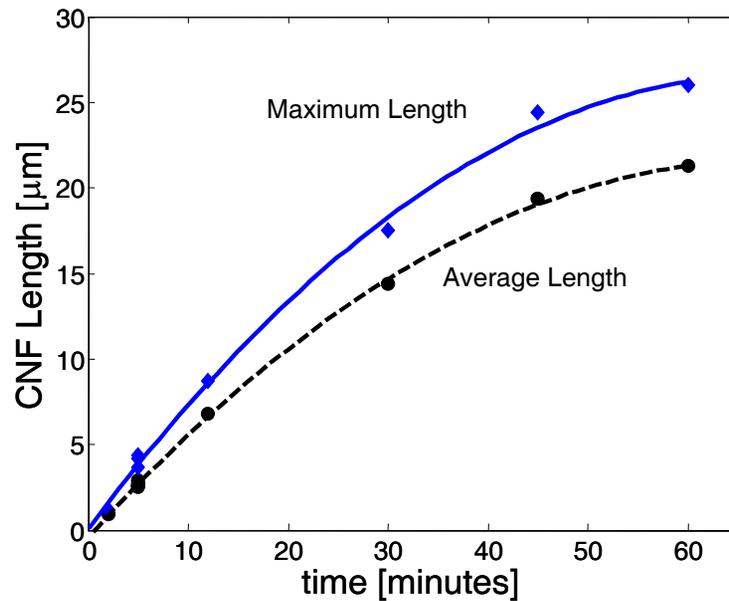
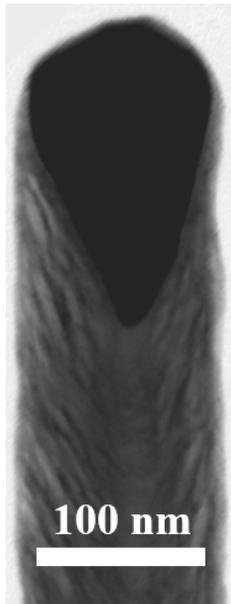
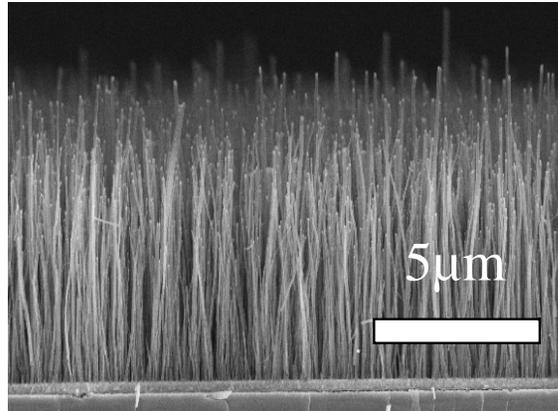
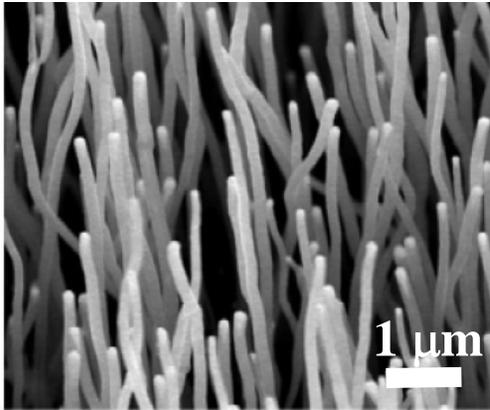
Li et al., *Appl. Phys. Lett.*, **82**, 2491 (2003)

Cruden et al., *J. Appl. Phys.*, **94**, 4070 (2003)





CNF Process Control





DC Characterization of CNF Vias

Collaborators: J. Li, A. Cassell, M. Meyyappan
Center for Advanced Aerospace Materials and Devices,
NASA Ames Research Center, Moffett Field, CA

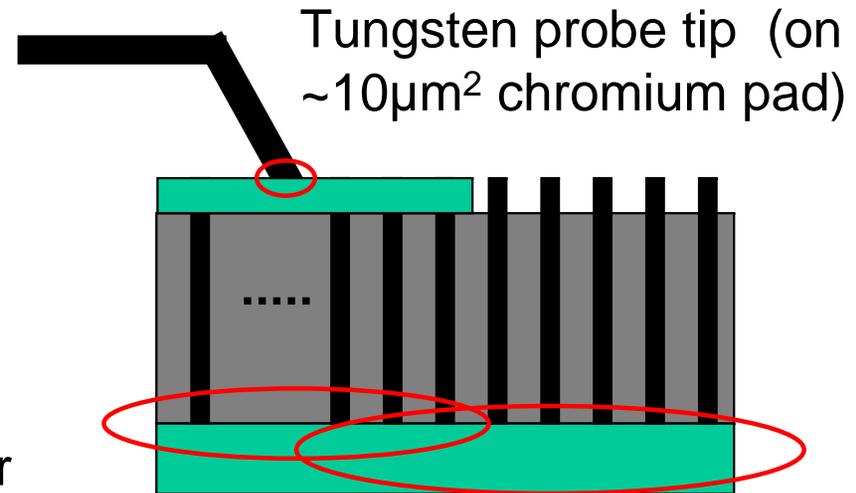
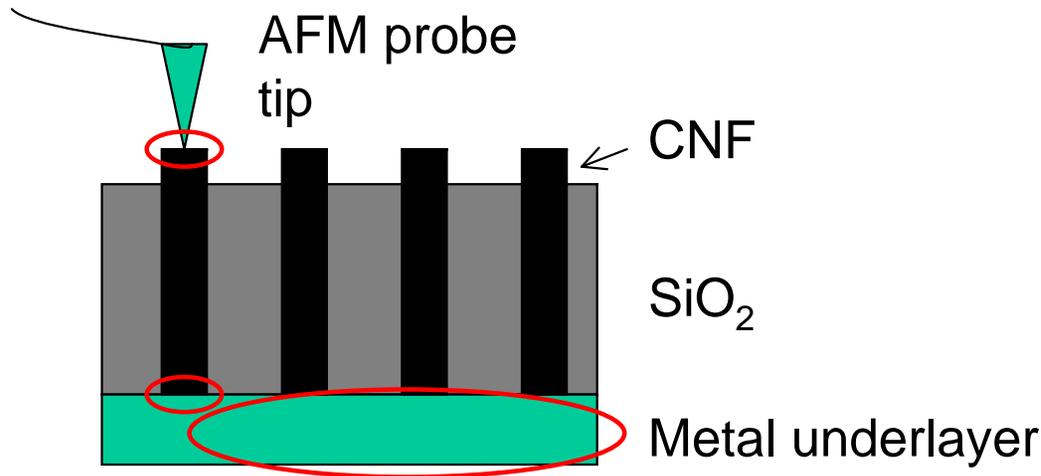


Collaborators: A. J. Austin
Center for Nanostructures,
Santa Clara University, Santa Clara, CA





Mechanisms of End-contact Resistance



Single CNF Resistance:

- AFM tip to CNF (contact)
- CNF to metal underlayer
- Metal underlayer sheet resistance

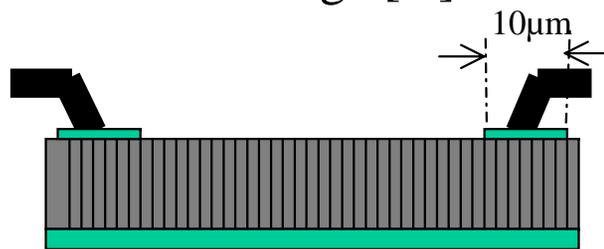
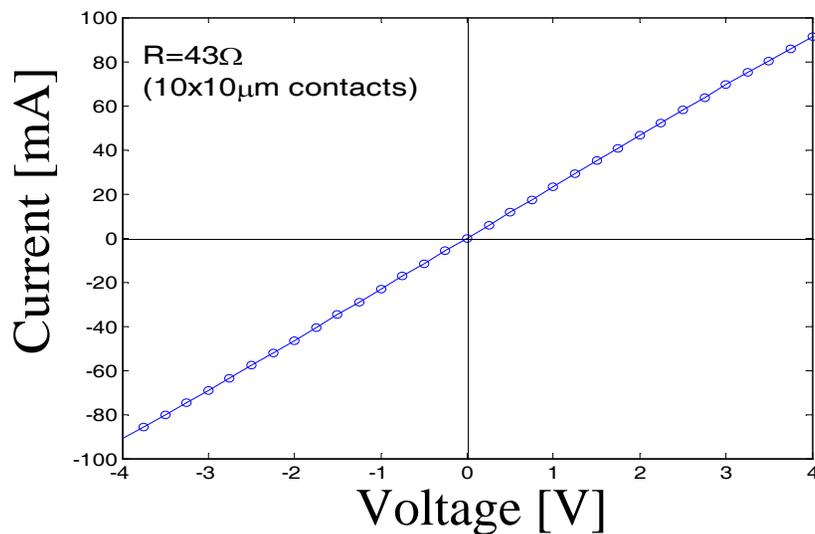
Parallel CNF Resistance:

- Probe tip/metal to CNF(contact)
- CNFs to metal underlayer
- Metal underlayer sheet resistance

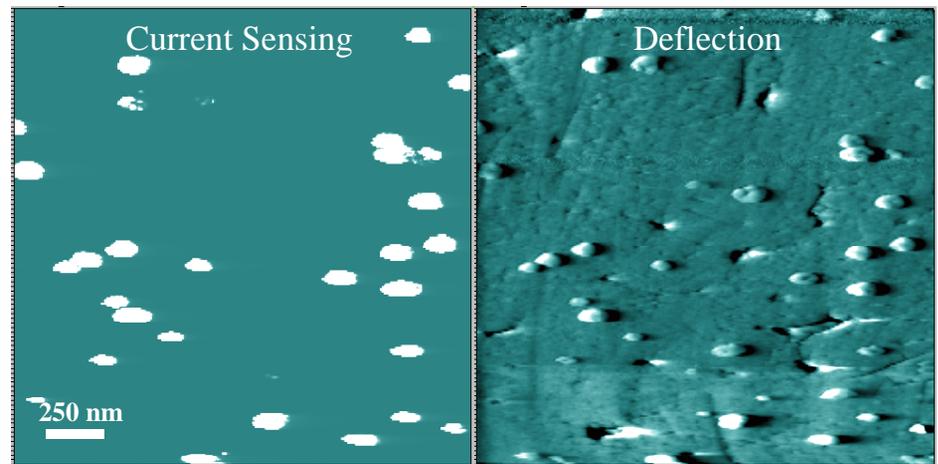


I-V Characteristics of CNF Array Vias

- A statistical approach can be taken for calculating resistance of a single CNF by measuring many CNFs in parallel



Ngo et al., *IEEE Trans. Nanotechnology* 3,
311-317 (2004)

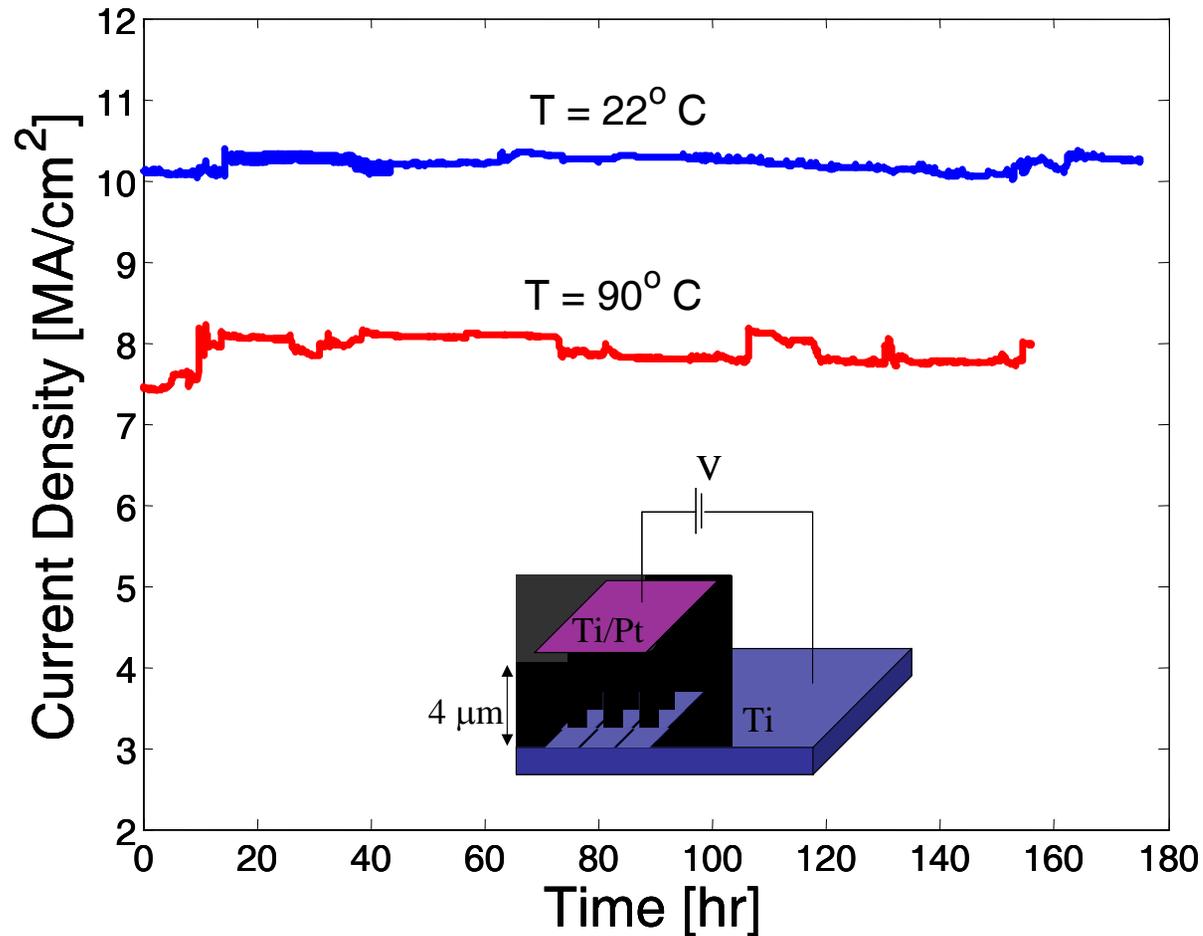


- Nanofiber diameters = 50-100nm
- ~5-6 CNF per $1\mu\text{m}^2$
- $100\mu\text{m}^2$ contains ~500-600 CNF

$R(\text{single CNF}) \approx 12\text{-}15\text{k}\Omega$



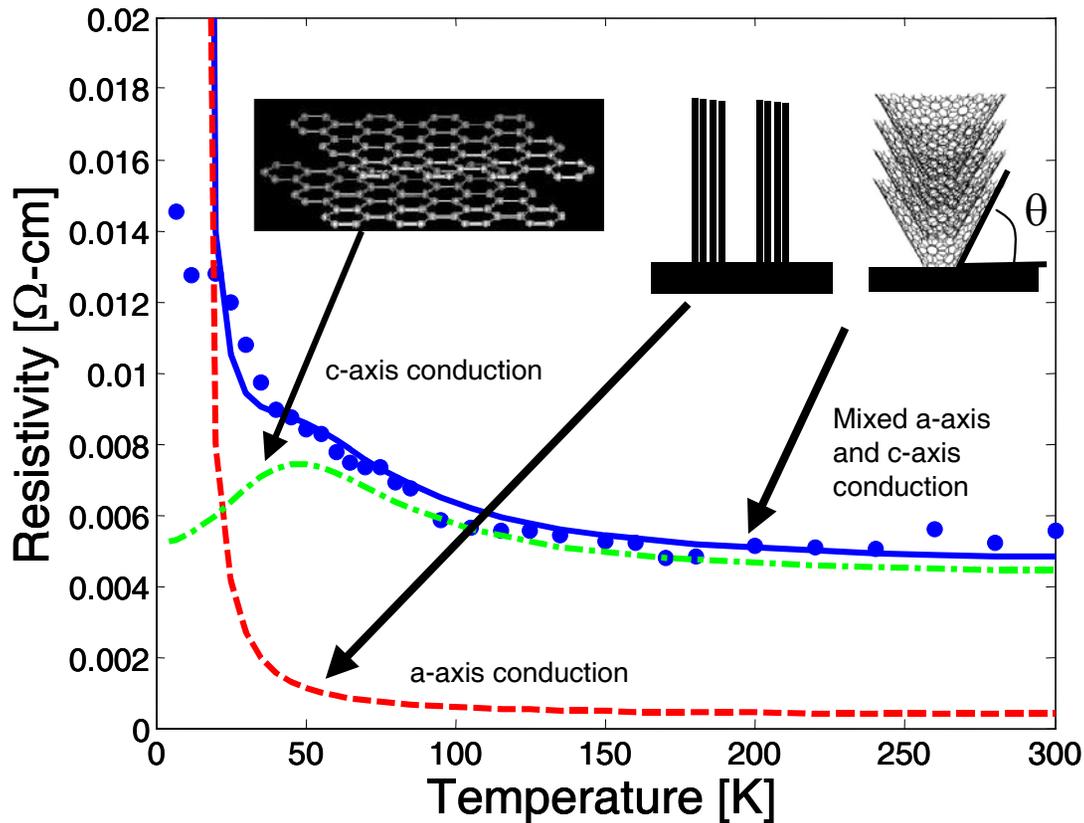
Reliability Measurement of CNF Via



ITRS Roadmap for 32 nm node: $J_{MAX} = 4 \text{ MA/cm}^2$



Modeling of Temperature-dependent Resistivity



Ngo et al., *Elec. Dev. Lett.* **27**, 221 (2005)

$$\rho(T) = \rho_0 + (\rho_a \sin^2 \theta) \exp\left(\frac{-E}{kT}\right) + (\rho_c \cos^2 \theta) \left(\frac{1}{gT^2 + \frac{b}{T^2 + c}} \right)$$

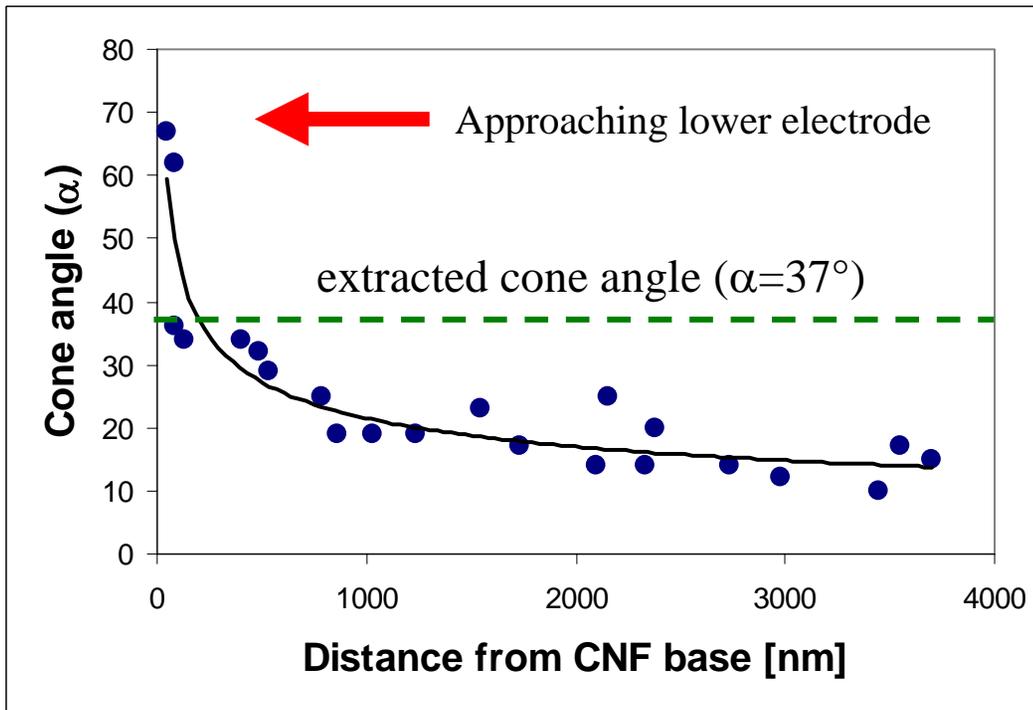
- Model incorporates both a-axis [1] and c-axis [2] graphite resistivity components
- Two fitting parameters, θ (complimentary cone angle) and ρ_0 (equilibrium resistivity) provide a good fit to the resistivity data
- All other model parameters assume pure graphite values from measurements [1,2]

[1] S. Ono et al., *J. Phys. Soc. Jap.* **21** (861) 1966

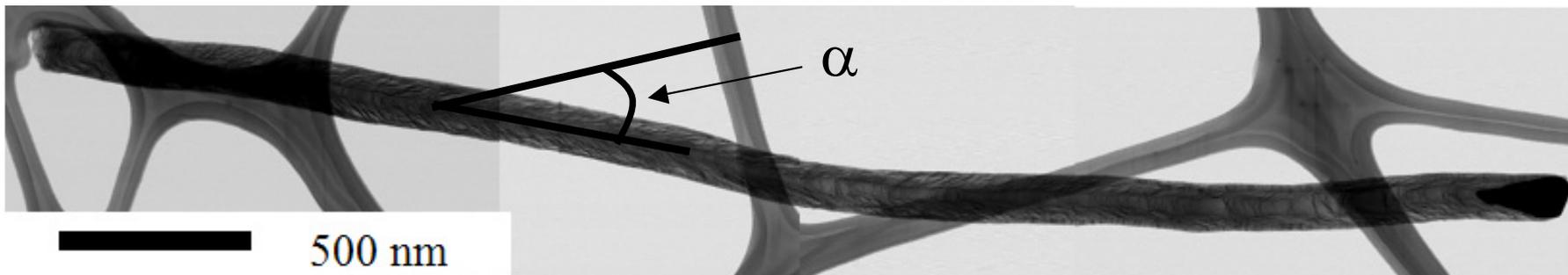
[2] C. Uher et al., *Phys. Rev. B* **35** (4463) 1987



Cone-angle variation



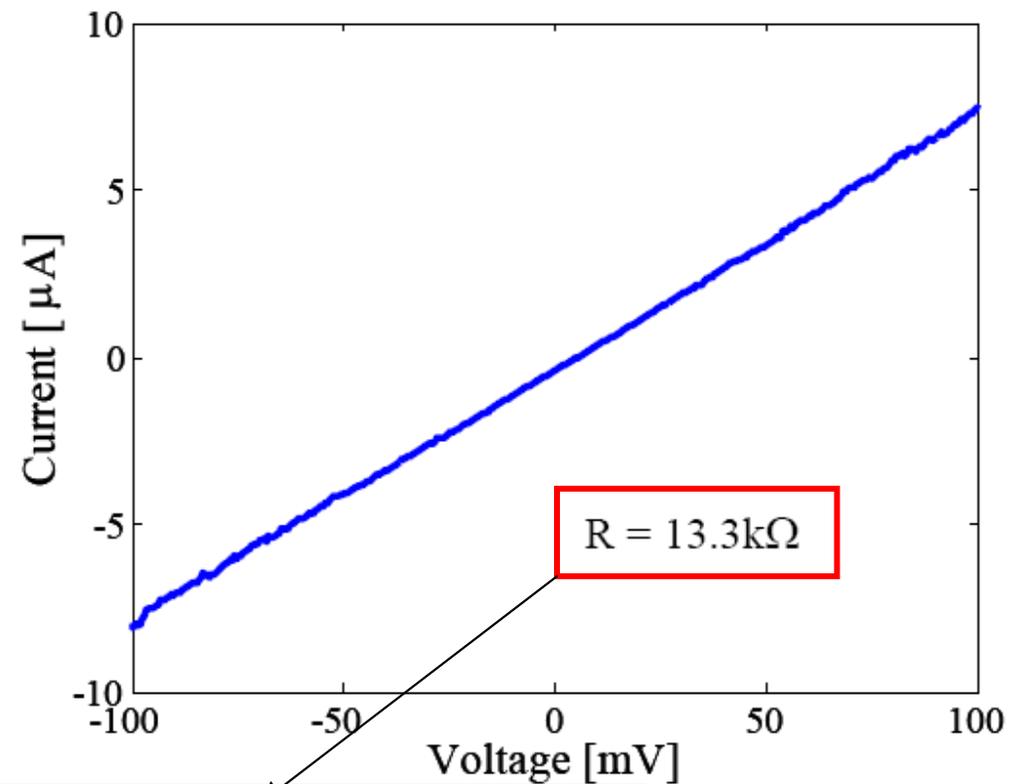
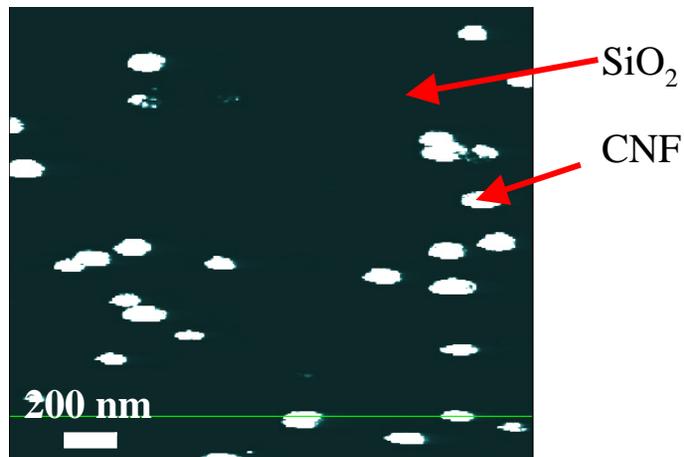
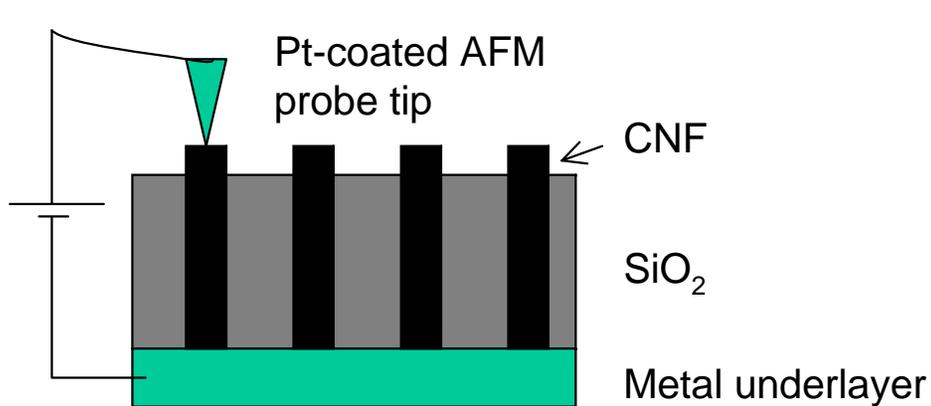
- Cone angle $\alpha=(90-\theta)=37^\circ$ extracted from the model equation
- Lower electrode influences resistivity, consistent with STEM analysis





I-V Characteristics of a single CNF

- Characterization of single CNFs using CSAFM confirms the result obtained from the statistical approach



Consistent with bulk measurement



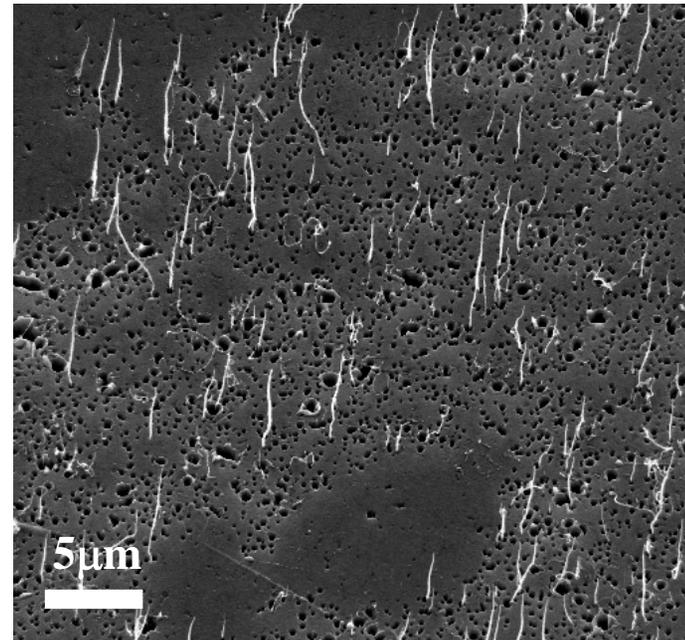
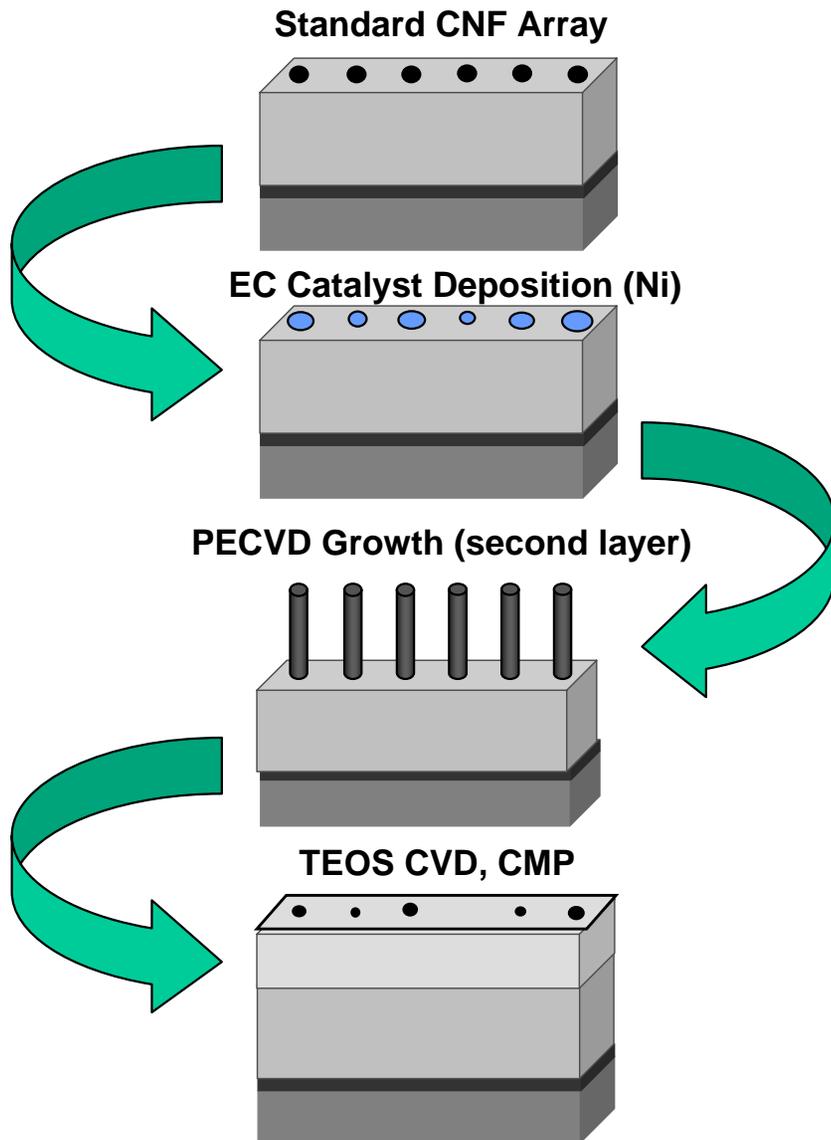
Multi-layer CNF Structures

Collaborators: J. Li, A. Cassell, M. Meyyappan
Center for Advanced Aerospace Materials and Devices,
NASA Ames Research Center, Moffett Field, CA

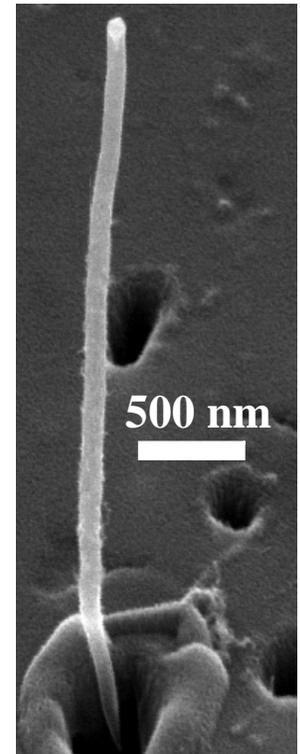




Process flow for CNF multi-layer growth



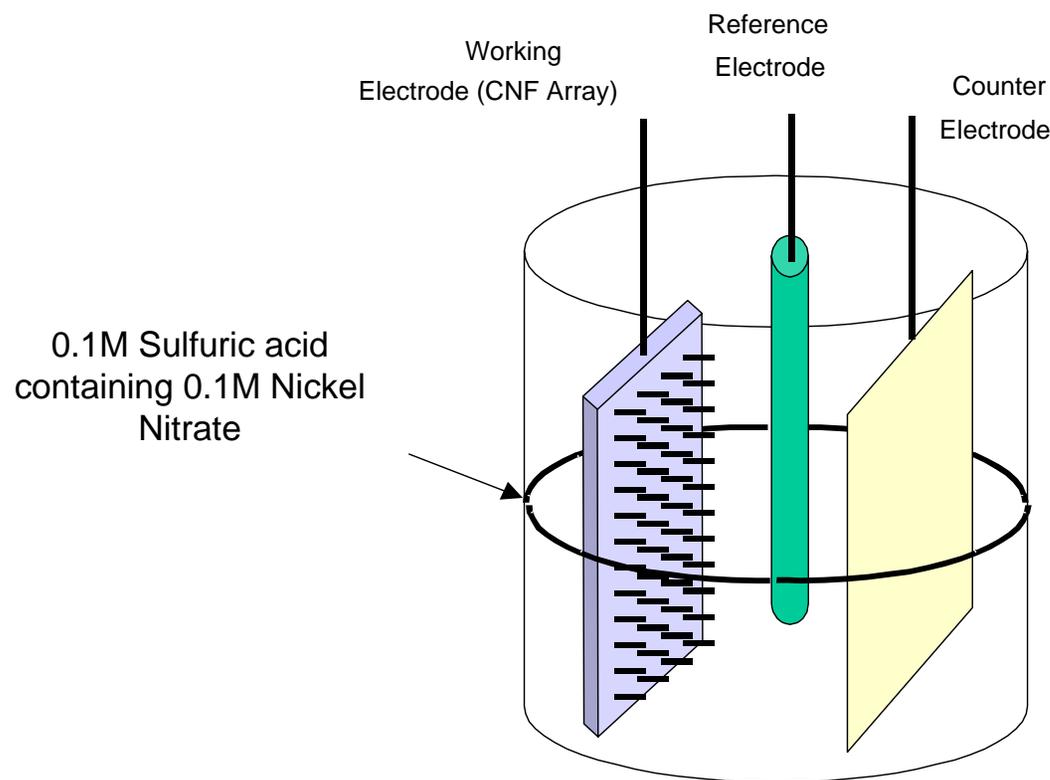
Post second-layer growth





Second-layer Catalyst Deposition (I)

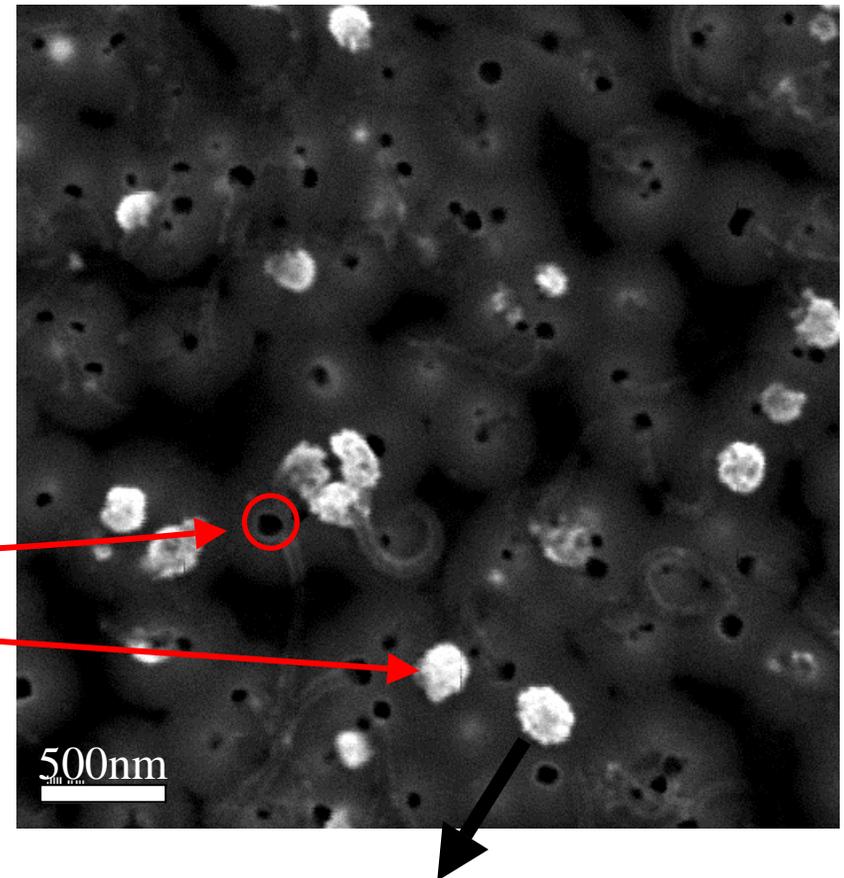
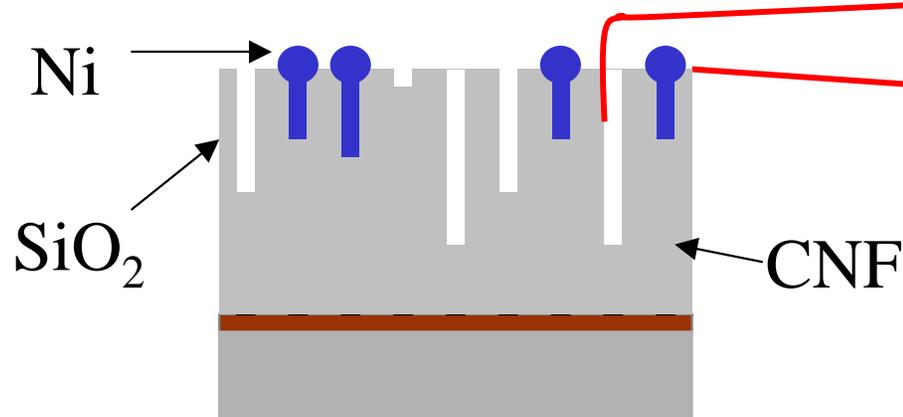
- Tubes are etched in NaOH solution to recess them into SiO₂ layer and expose -OH and -COOH groups at CNF ends
- Provides a good carbon electrode for selective Ni catalyst growth
- Deposition is optimized at -0.70V vs. SCE for 45-60 minutes





Second-layer Catalyst Deposition (II)

- Not all first layer nanofibers can form heterojunctions
- Some nanofibers are recessed deep in SiO_2 after NaOH etch (preventing Ni deposition)



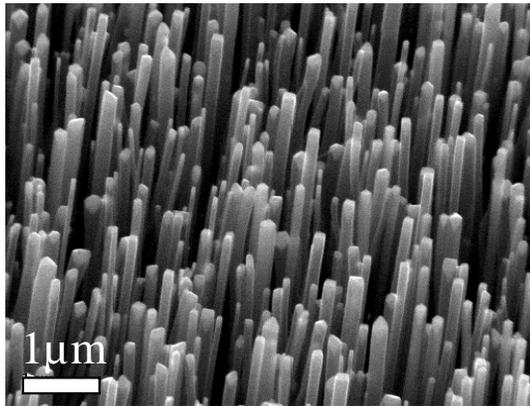
Average Ni cluster size: 200nm



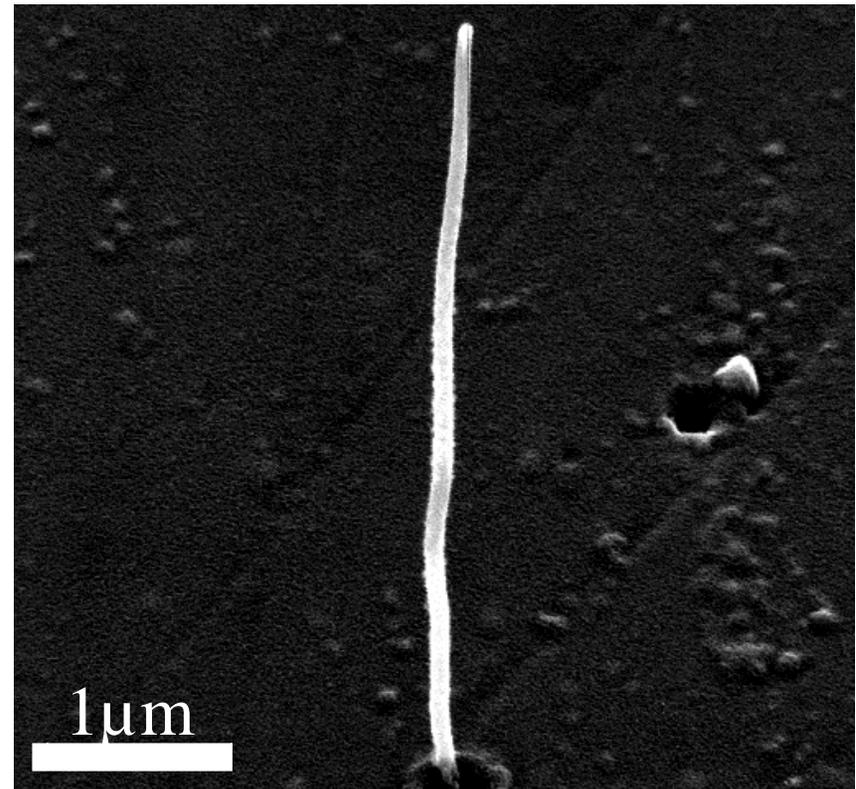
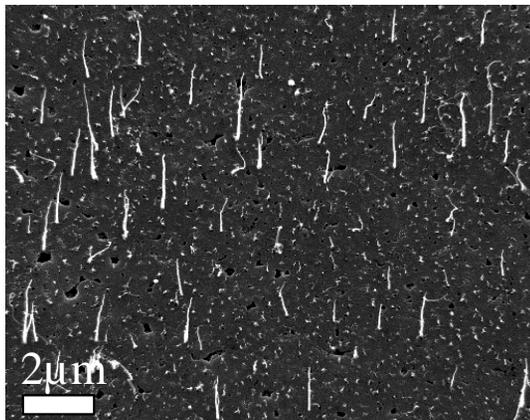
Second-layer Nanofiber Growth (I)

- Same PECVD growth conditions were used for second layer

First-layer CNF array growth



Second-layer CNF array growth



Second-layer Nanofiber

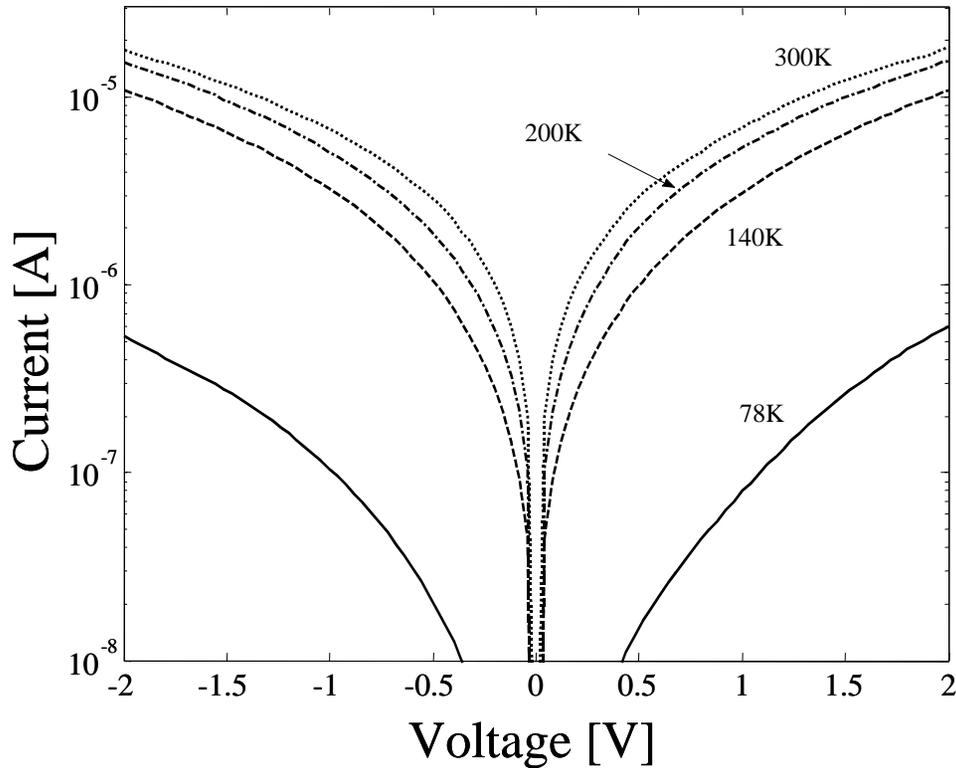


Summary of CNF Multi-layer Growth

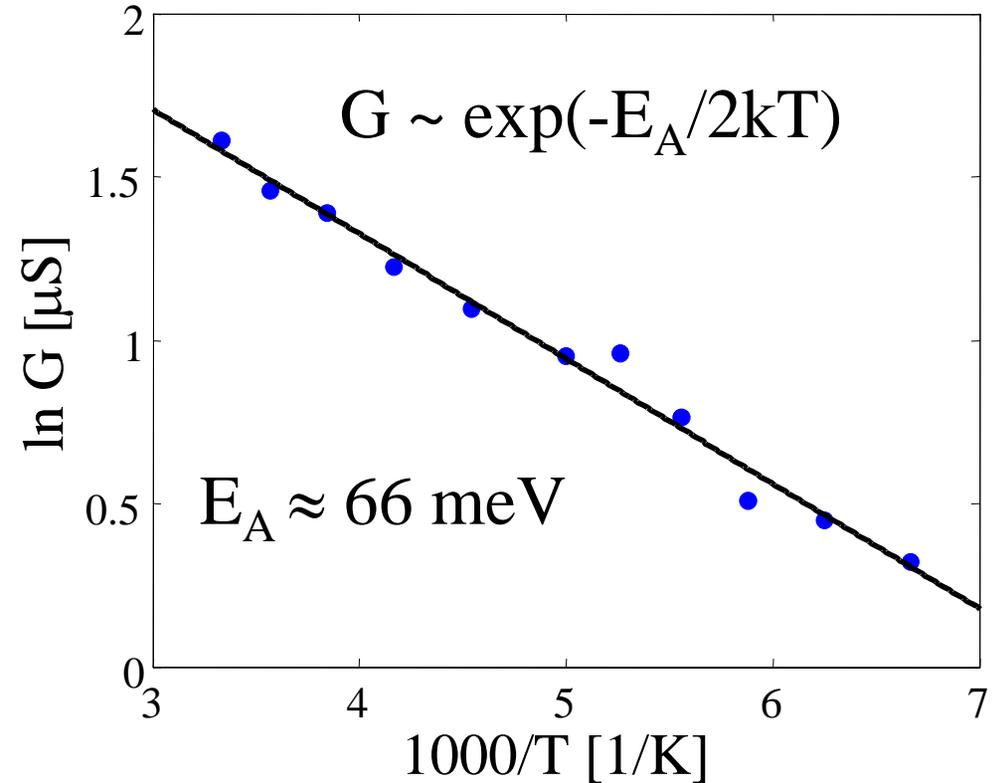
- Ni cluster size can be well controlled using nickel nitrate $\text{Ni}(\text{NO}_3)_2$
 - Parameters: deposition potential, deposition time, nickel concentration
- Morphology of second-layer nanofibers depends on Ni cluster geometry
- Density of second-layer nanofibers is low



I-V Characteristics of Multi-layer CNF Array



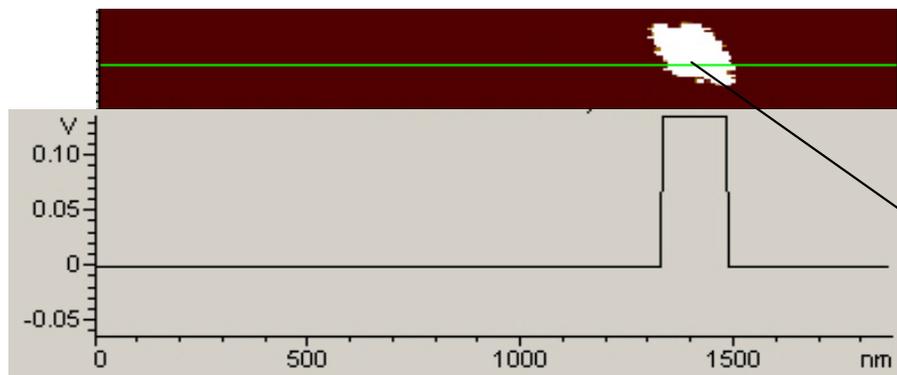
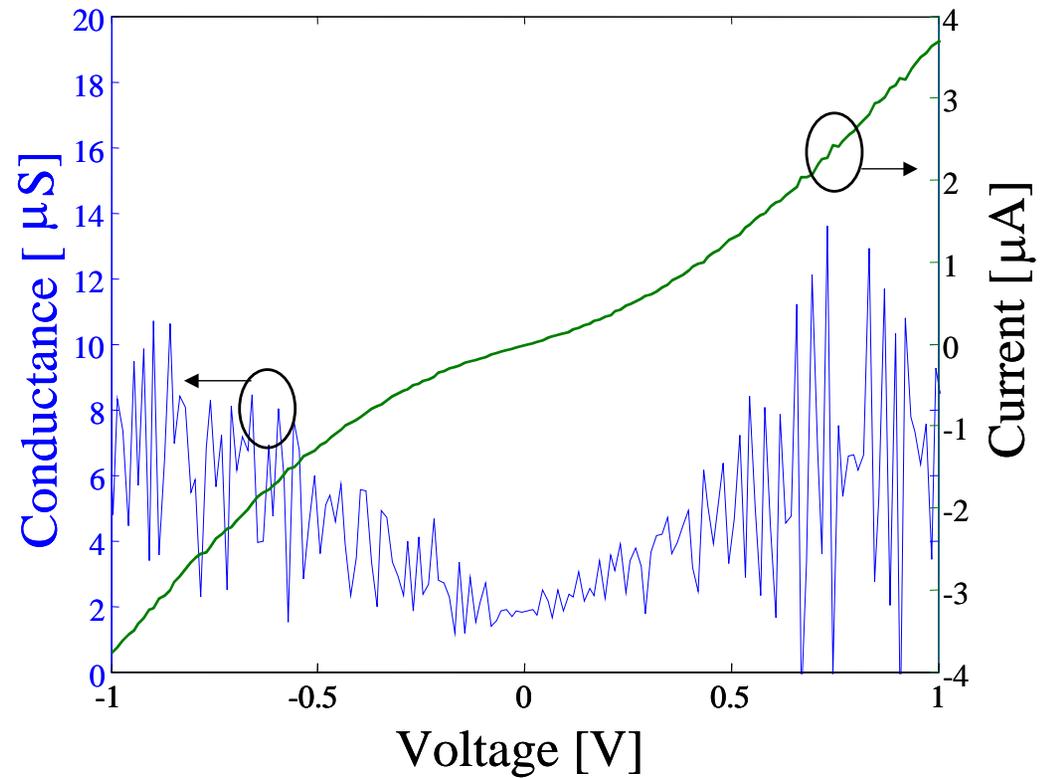
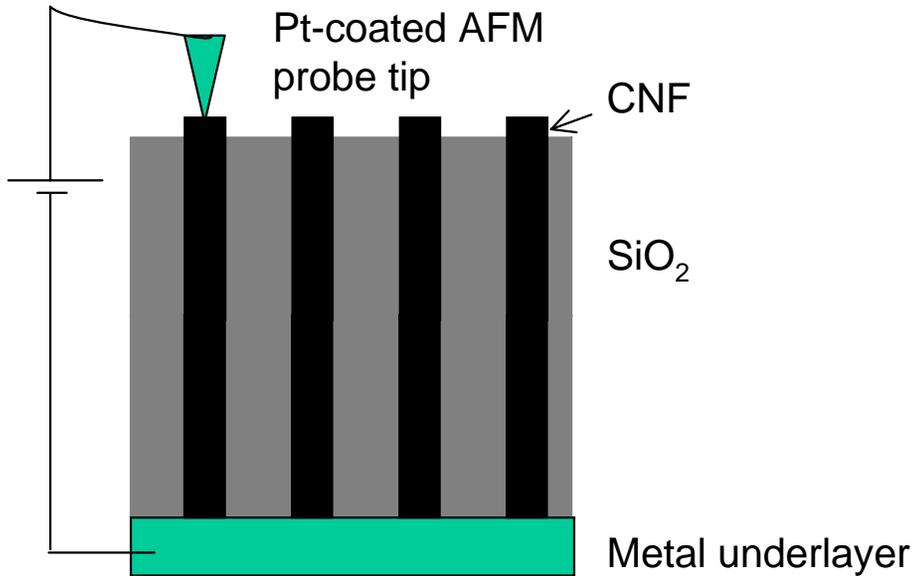
Tunnel junction-like behavior of Multi-layer CNF Array



Temperature dependence of differential conductance G at $V=0$



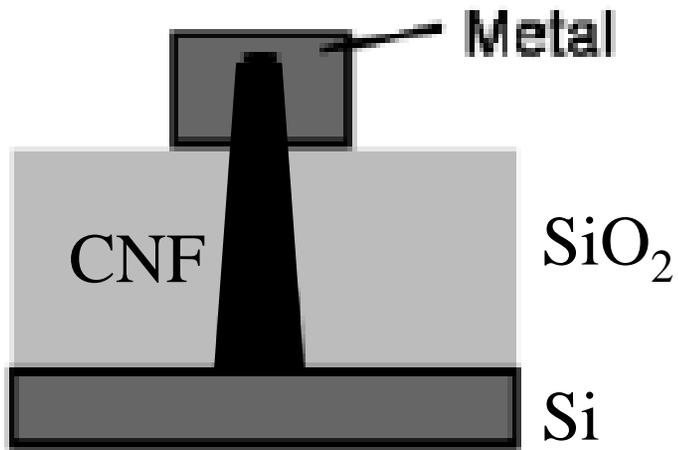
I-V Characteristics of Single Multi-layer CNF



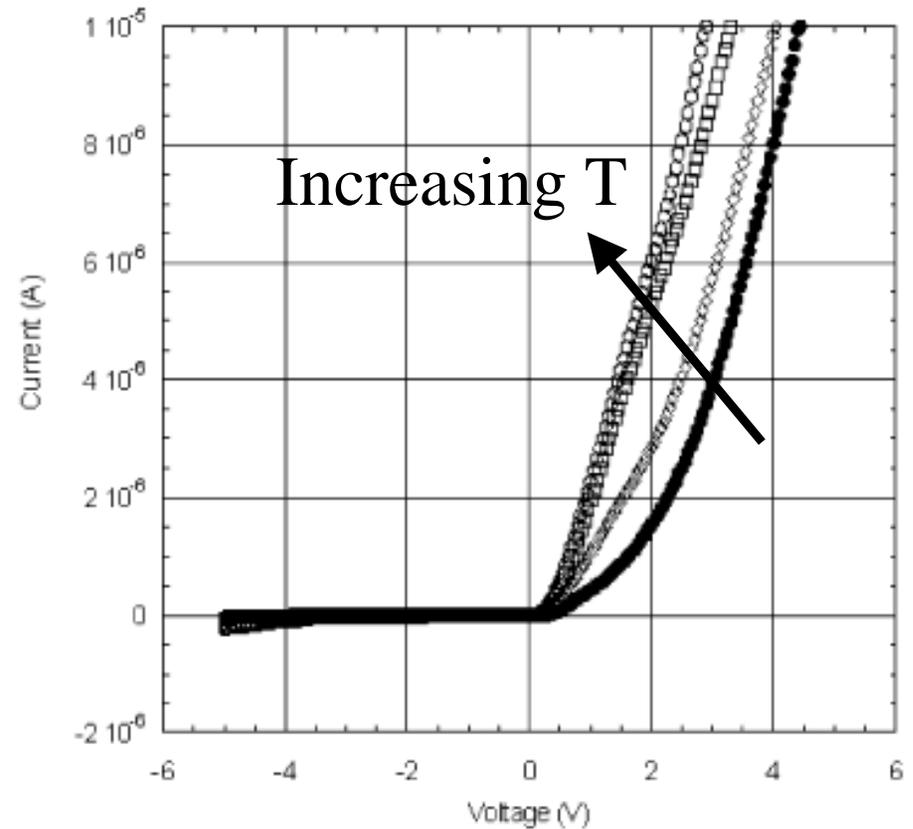
Second layer CNF diameter \approx 200 nm



Potential Multi-layer CNF devices



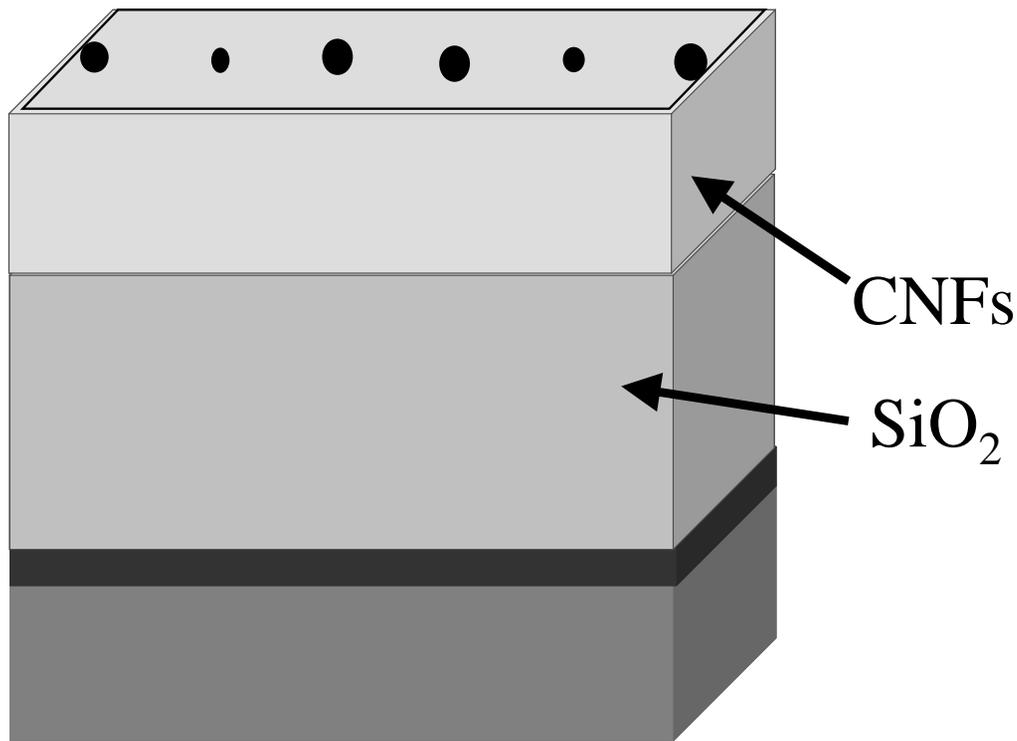
Si-based Schottky Barrier Diode



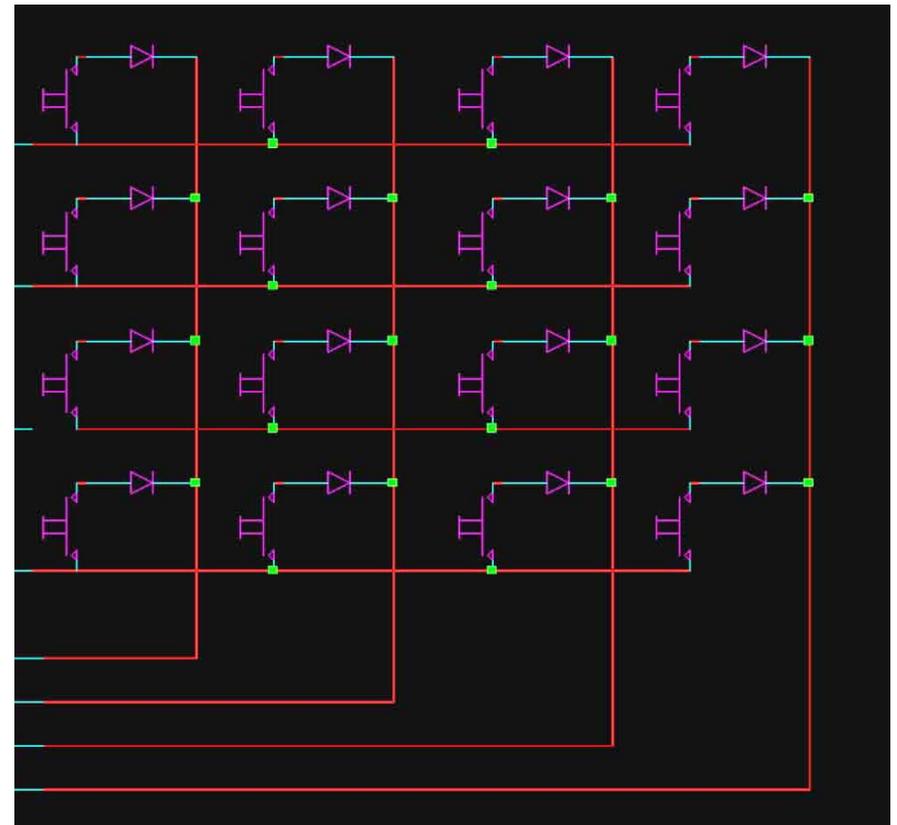
X. Yang et al., *Nano Lett.* **3**, 1751 (2003)



Potential Multi-layer CNF devices



CNF diode array





TEM/STEM Analysis of Individual CNFs

Collaborators: Y. Ominami, M. Suzuki
Hitachi High Technologies America (HHTA)
Pleasanton, CA

Collaborators: V. R. Radmilovic
National Center for Electron Microscopy (NCEM)
Lawrence Berkeley National Laboratory
Berkeley, CA

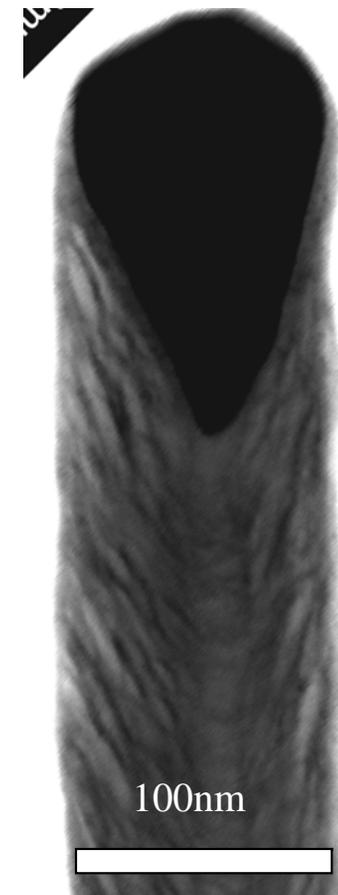
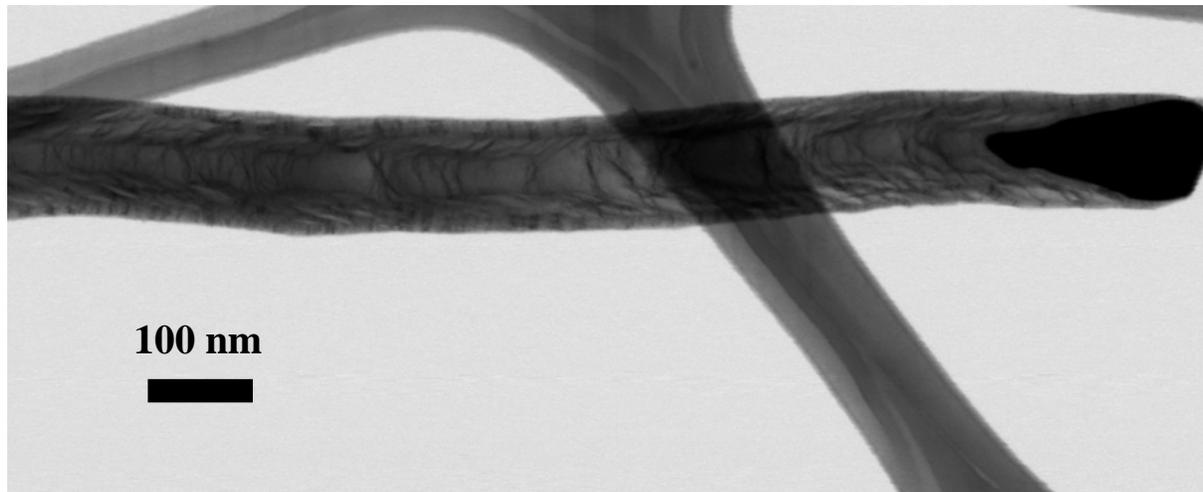
HITACHI
Inspire the Next





STEM analysis of Ni-catalyzed CNFs (I)

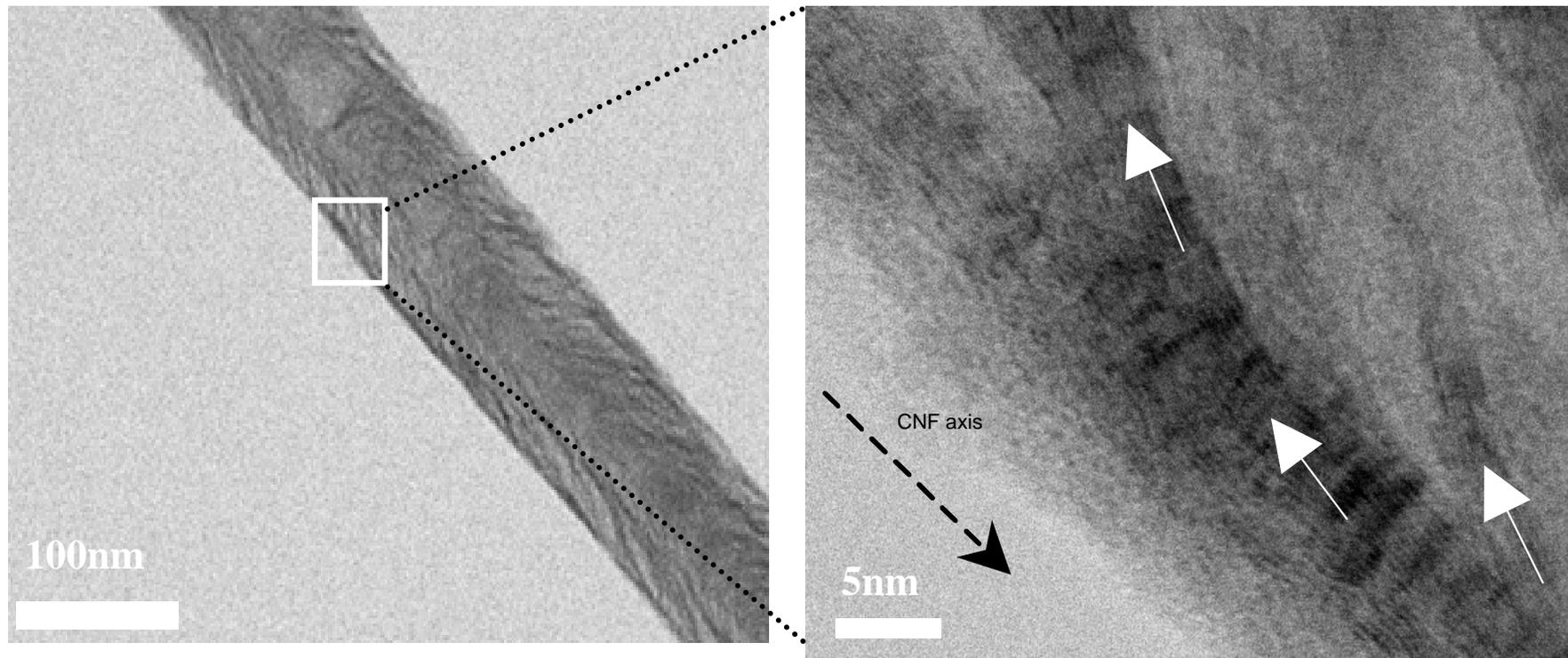
- Nickel-catalyzed CNFs show stacked cone morphology
- Scanning Transmission Electron Microscopy (STEM) using Hitachi S-4800





STEM analysis of Ni-catalyzed CNFs (II)

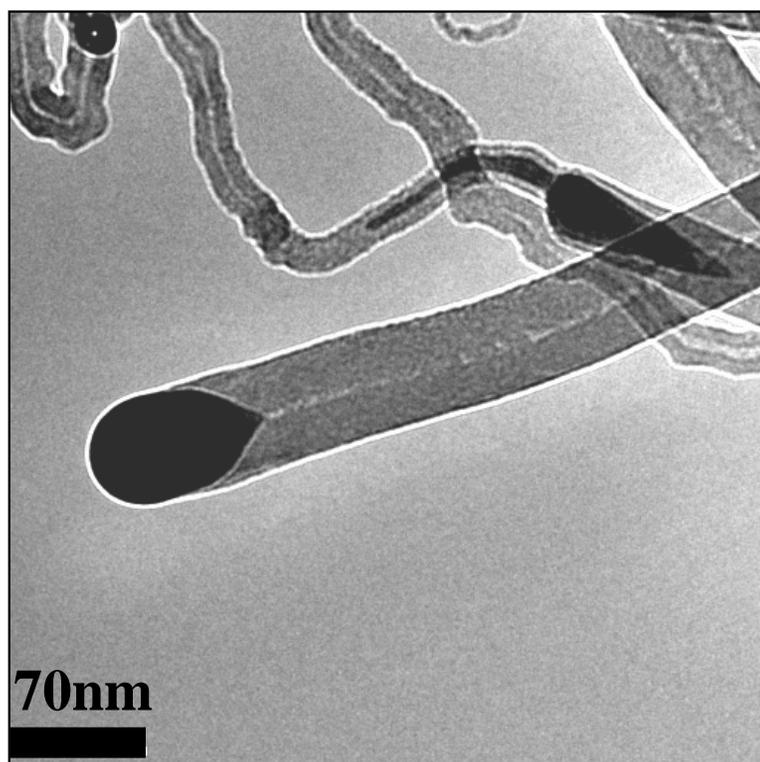
- High-resolution STEM shows stacked cone morphology observed on the outer regions of CNF



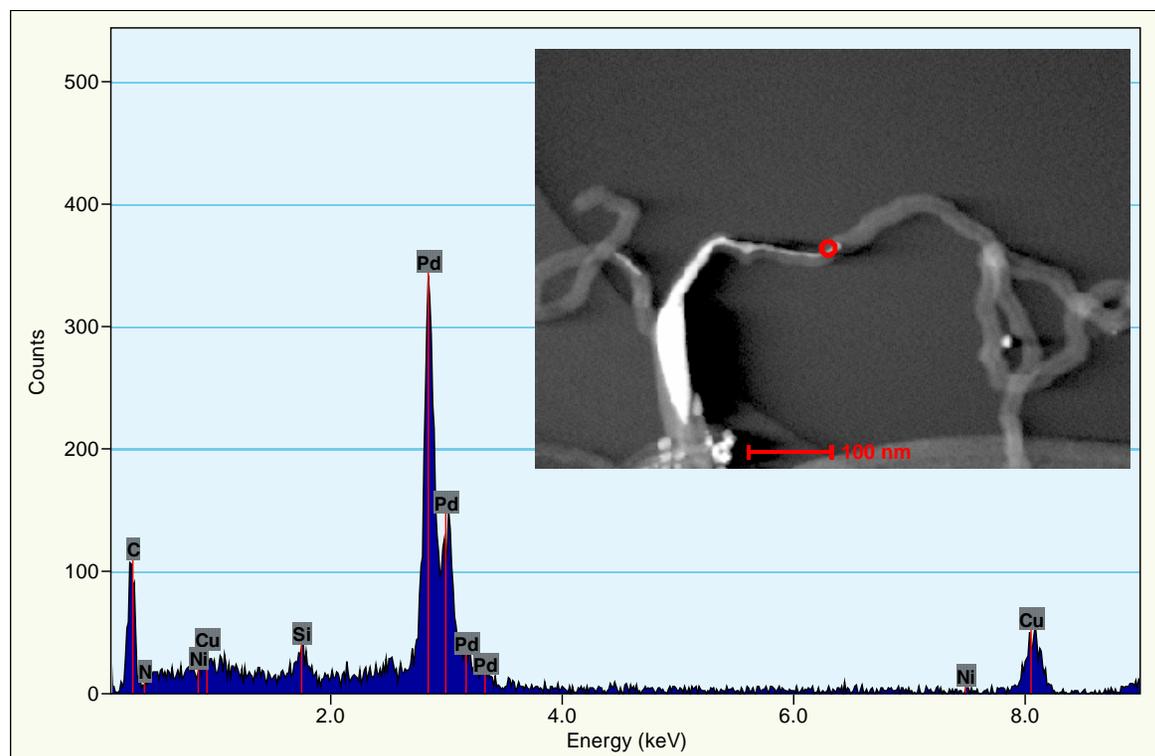


TEM analysis of Pd-catalyzed CNFs

- Secondary growth anomalies in Pd-catalyzed CNFs
 - [Ngo et al., *Carbon*, in press (2006)]



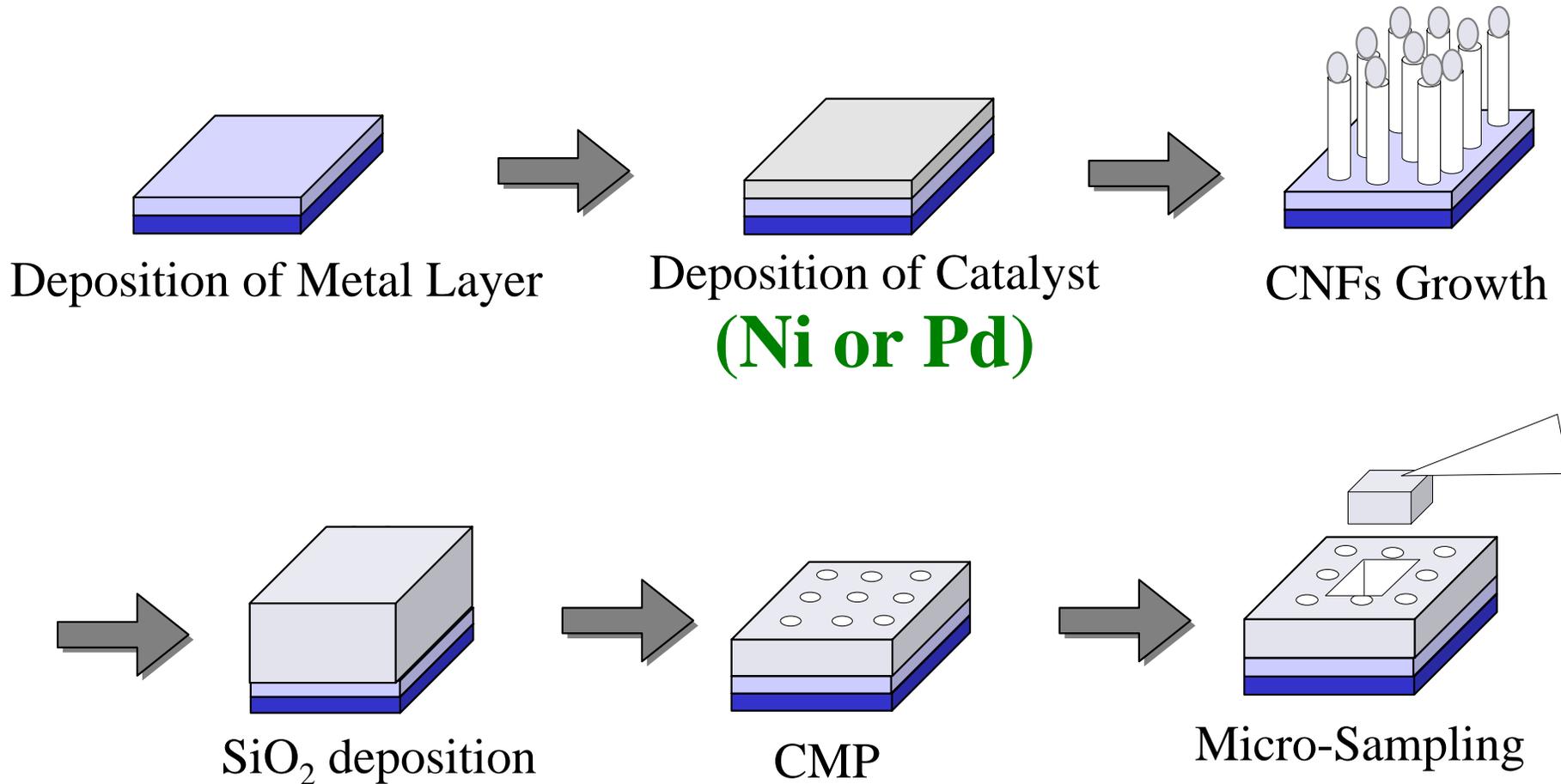
TEM image of secondary CNF growth



Energy Dispersive X-Ray Spectrum (EDX)

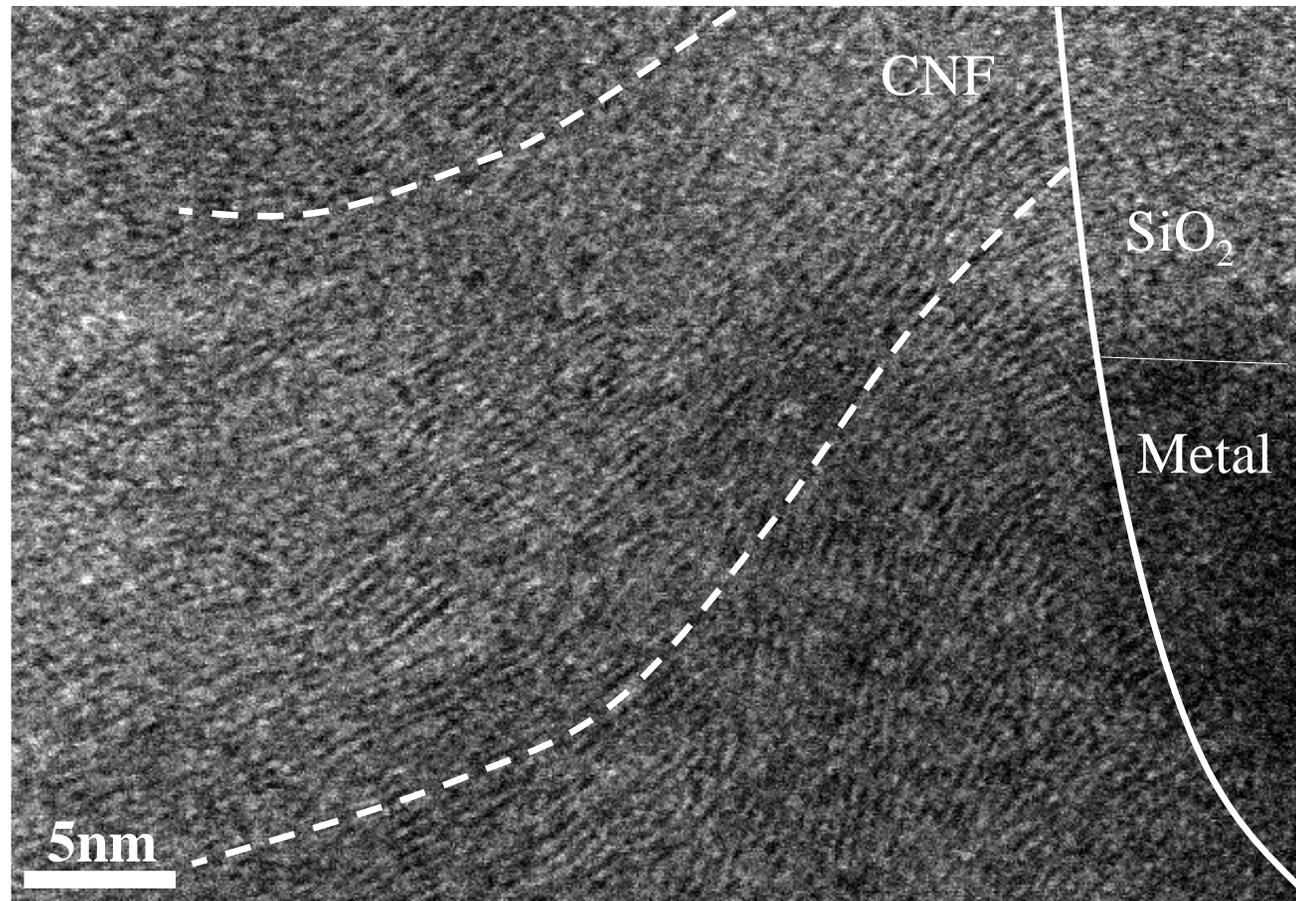
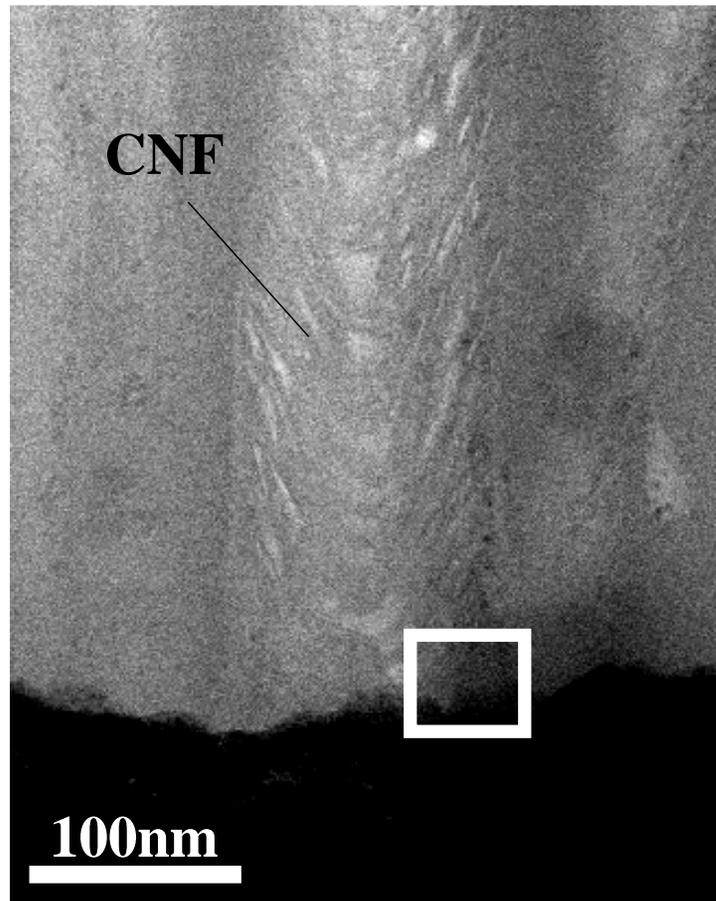


Sample Preparation





STEM (HD-2300) Images

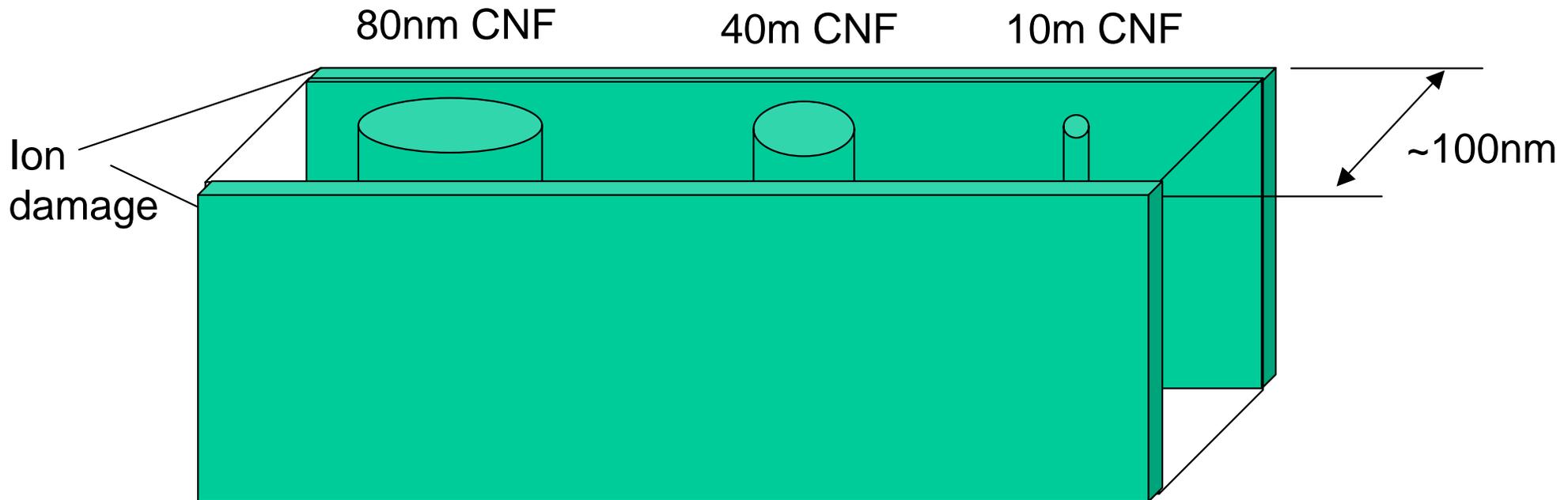


The interface images of Ni-catalyzed CNF

Y. Ominami et al, *Appl. Phys. Lett.* **87**, 233105 (2005)



Issues with sample preparation

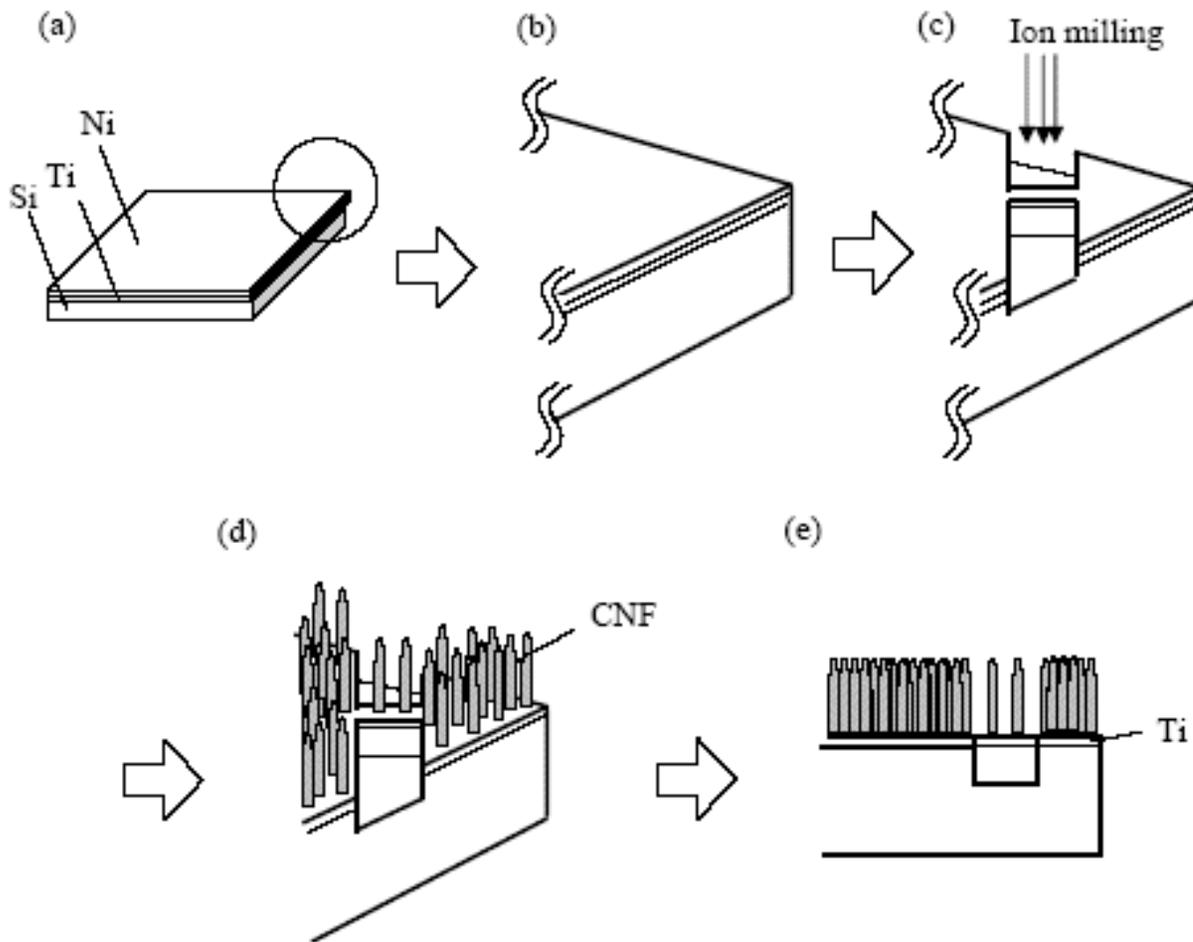


- TEM images are constructed by a convolution of transmitted electrons through both CNFs and materials around CNFs.
- Ion beam may destroy CNF structure in the process to make a thin foil (100nm or less) due to ion scattering in the foil.
- CNFs cannot be easily found in a prepared thin foil due to their small diameters.



Solution

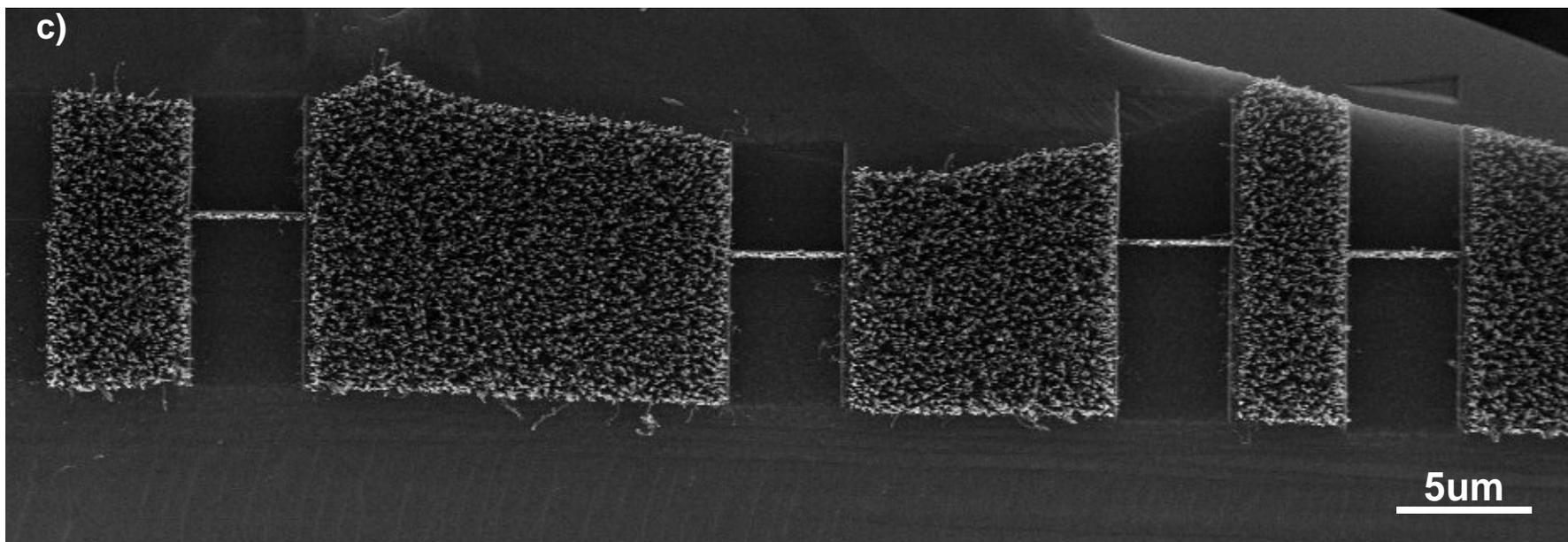
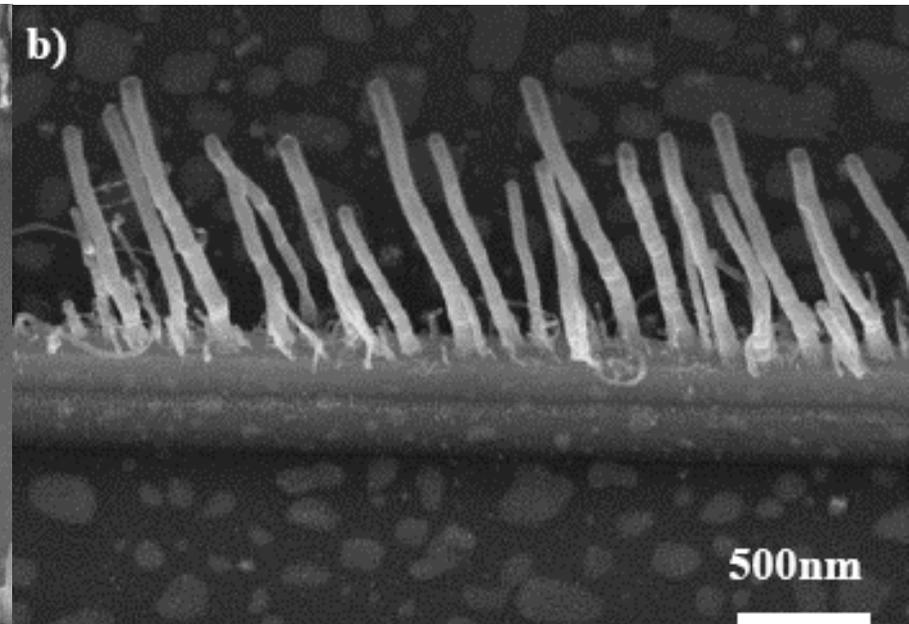
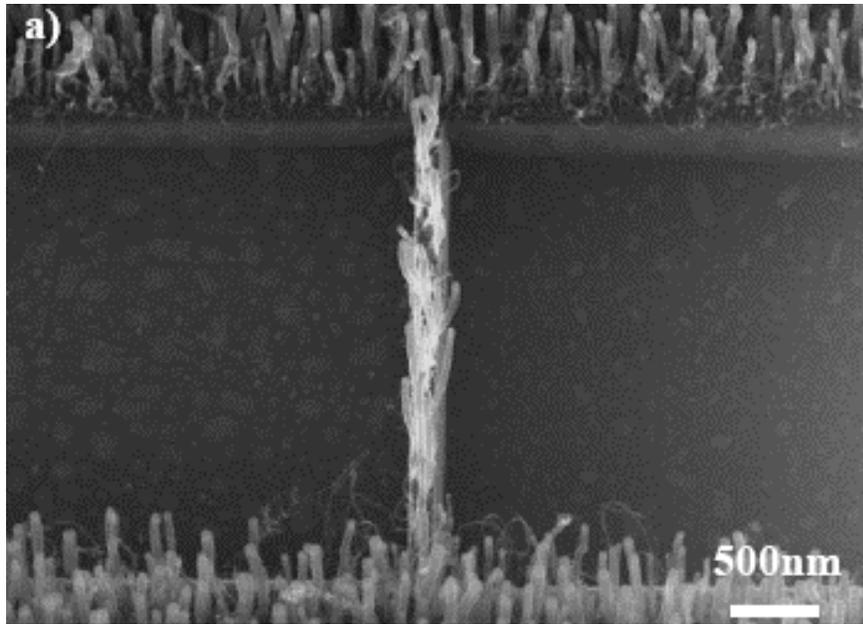
“Bottom-up sample preparation”



Ion milling **before** CNF growth

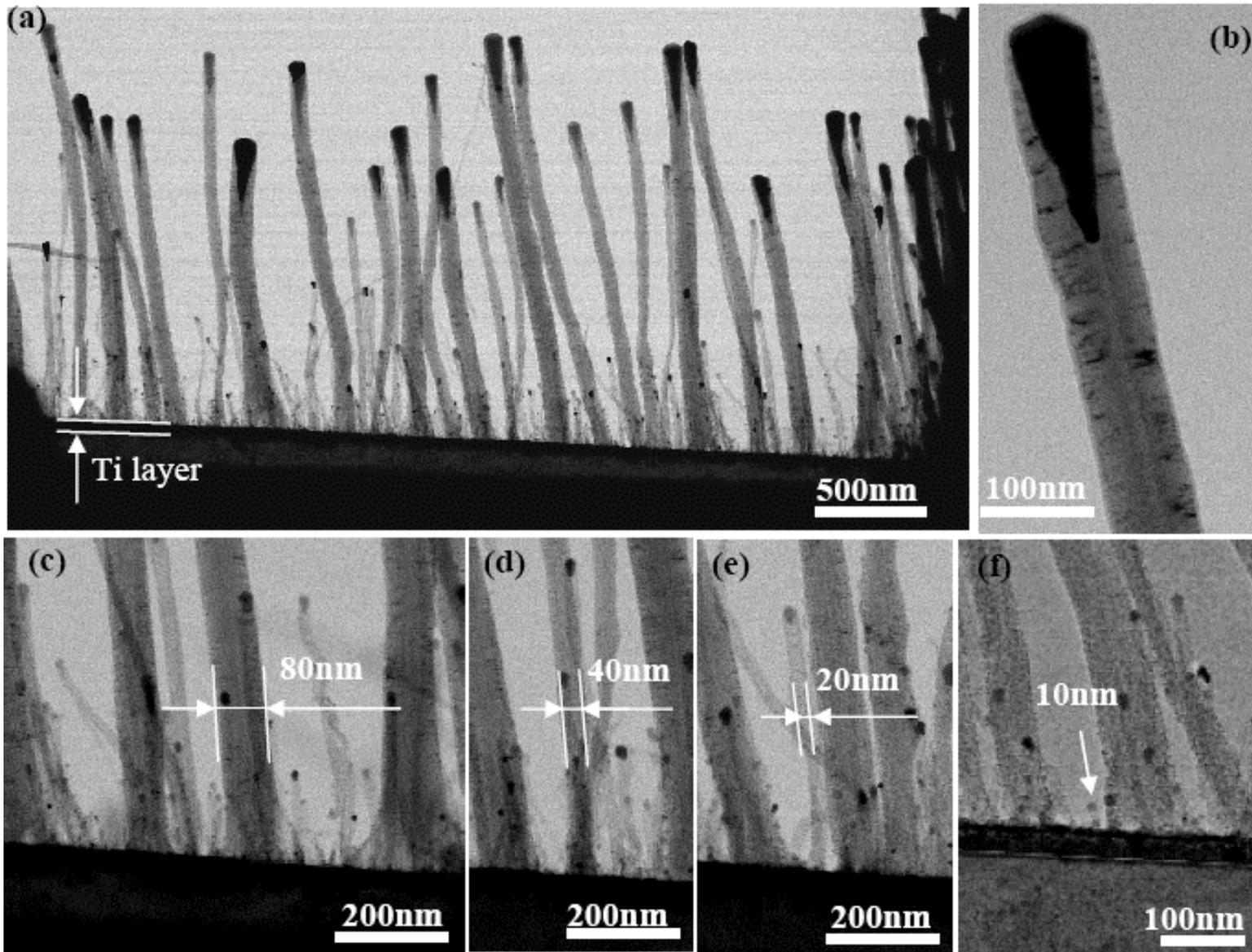
- No protective material around CNFs

- Applicable to other vertically grown materials, such as nanowires



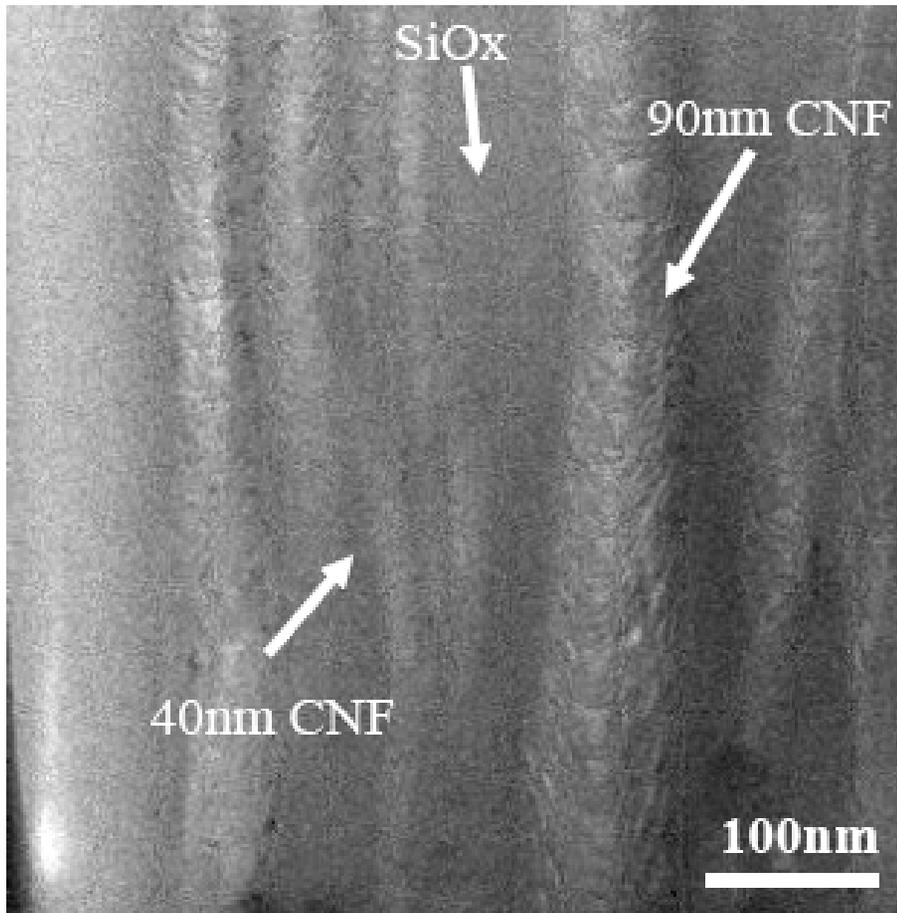


STEM images of CNFs on narrow strip

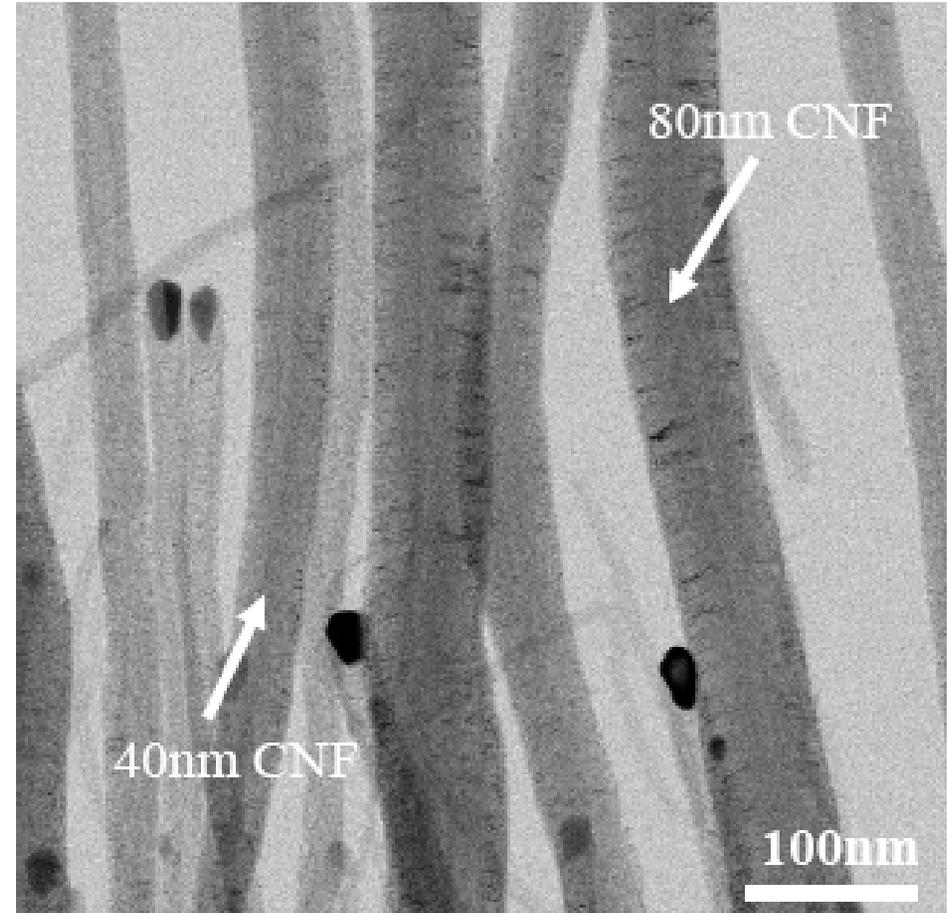




Comparison of preparation methods



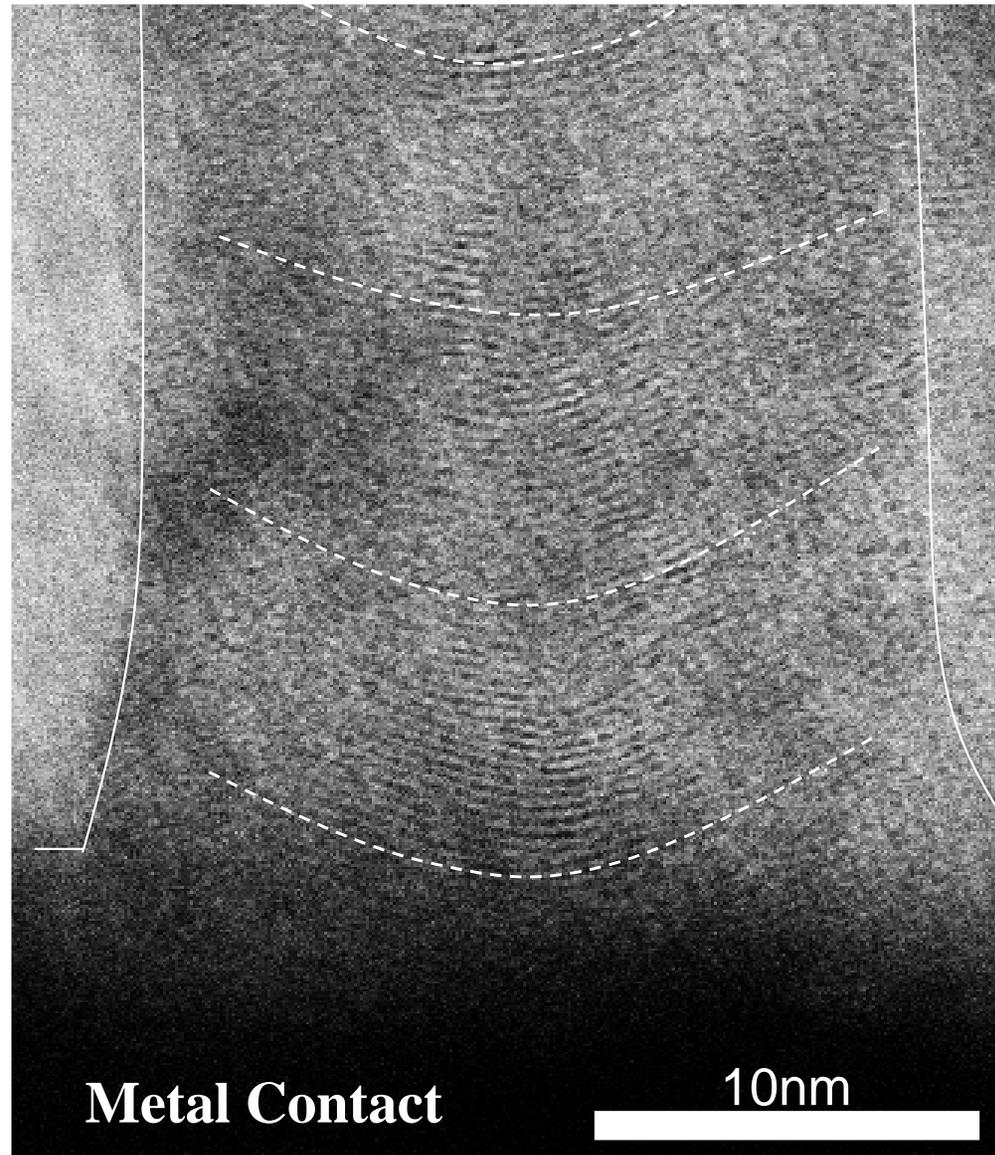
**Sample prepared by Conventional
Sample Preparation**



**Sample prepared by Bottom-up
Sample Preparation**

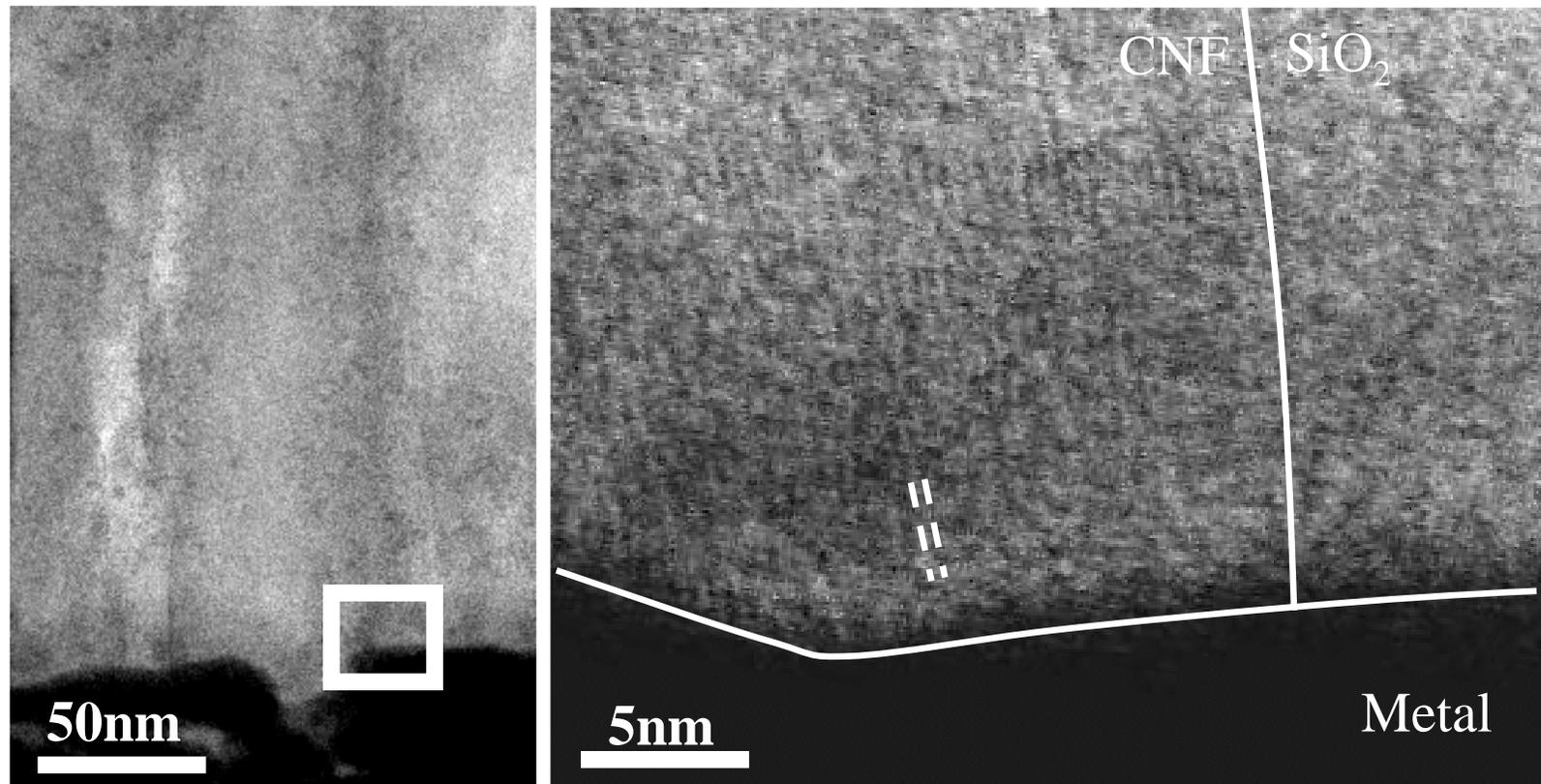


CNF-metal contact interface





STEM (HD-2300) Images of Pd-catalyzed CNF



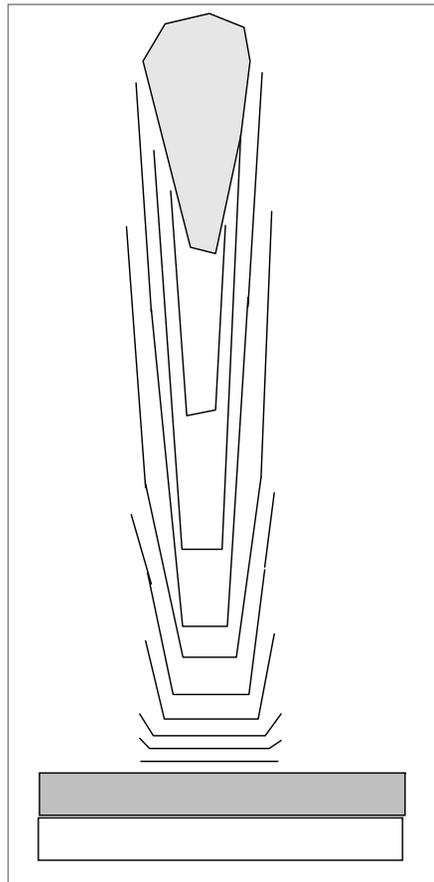
The interface images of Pd-catalyzed CNF

Y. Ominami et al, *Appl. Phys. Lett.* **87**, 233105 (2005)



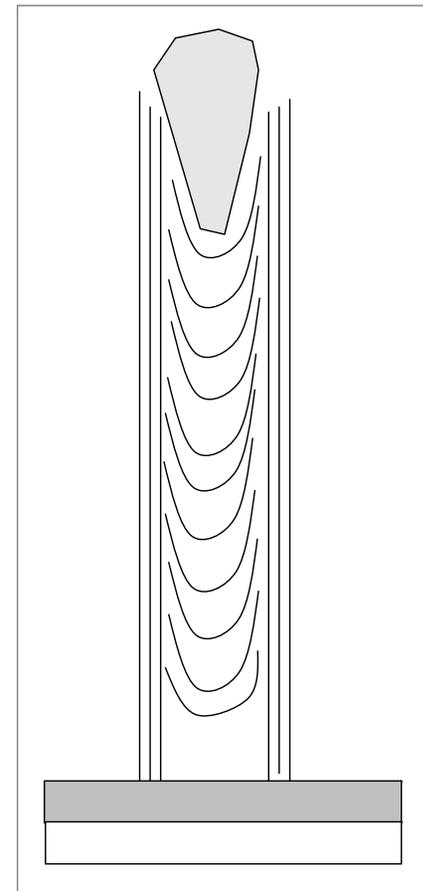
Structural Model

Ni-catalyzed CNF



Ni-catalyzed CNFs have stacked graphitic layers near the CNF-metal interface.

Pd-catalyzed CNF

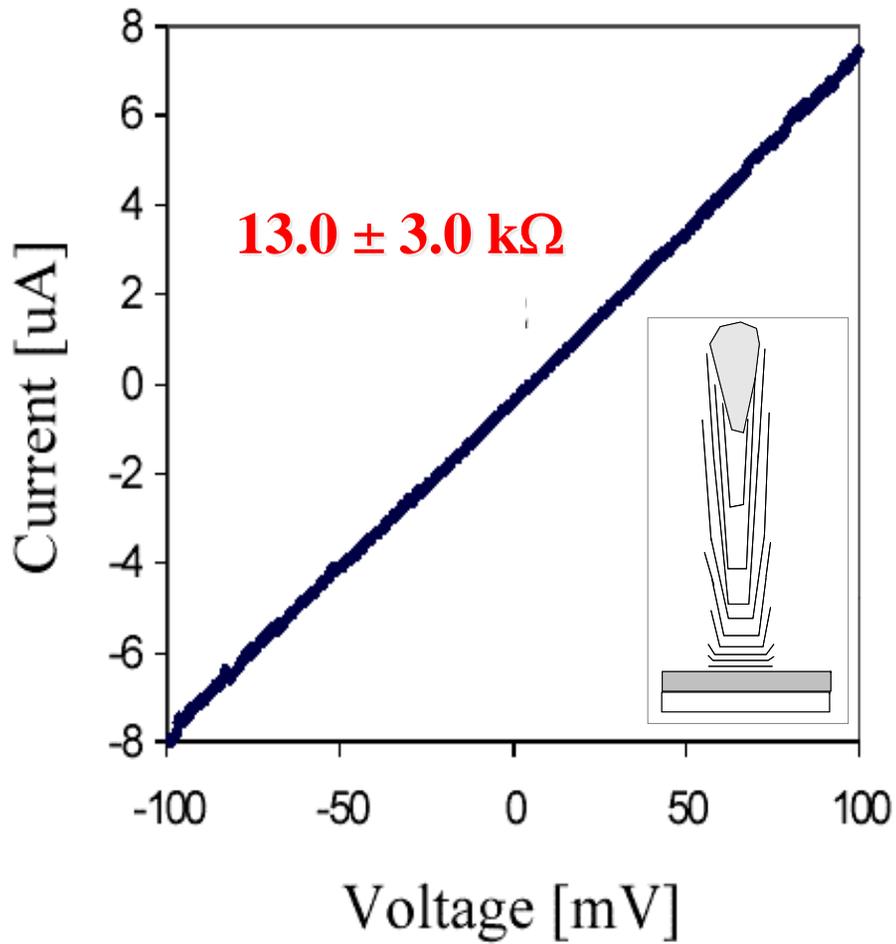


Pd-catalyzed CNFs have MW-like structure spanning the entire CNF.

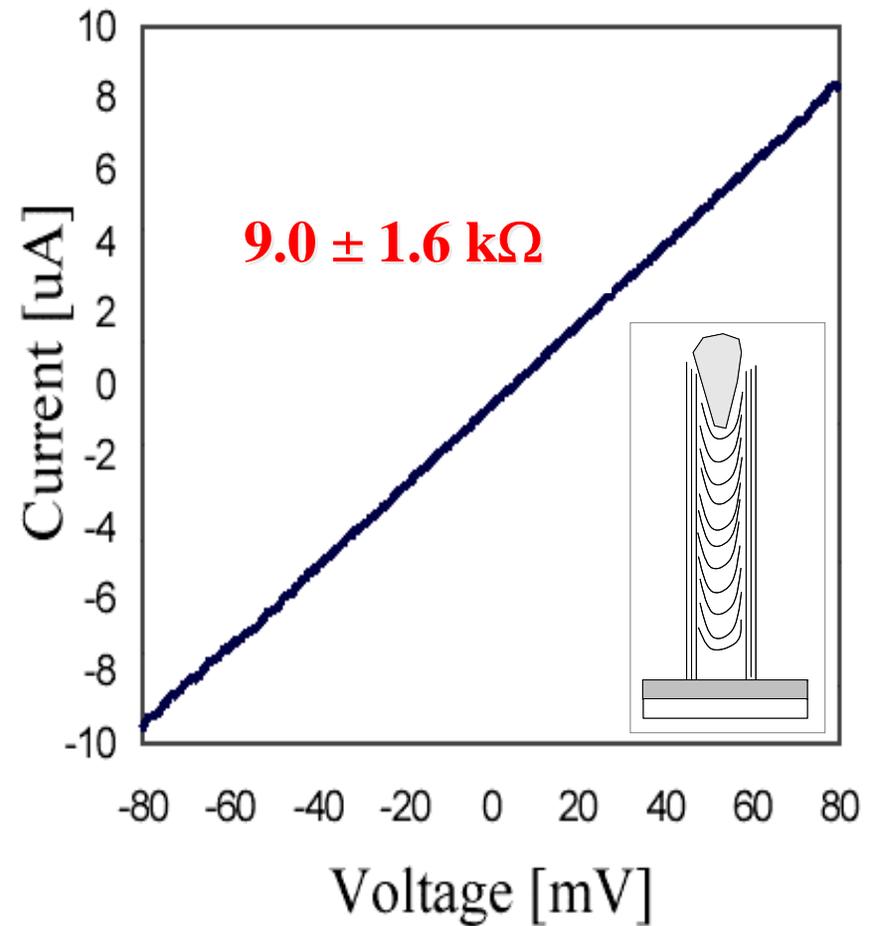


Resistance measurement using AFM

Ni-catalyzed CNF



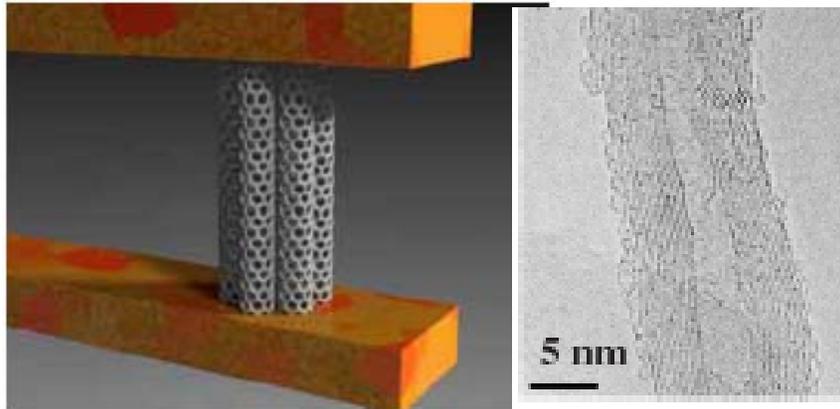
Pd-catalyzed CNF



Ominami et al., *Proc. IEEE NANO* vol. 2, 665 (2005)

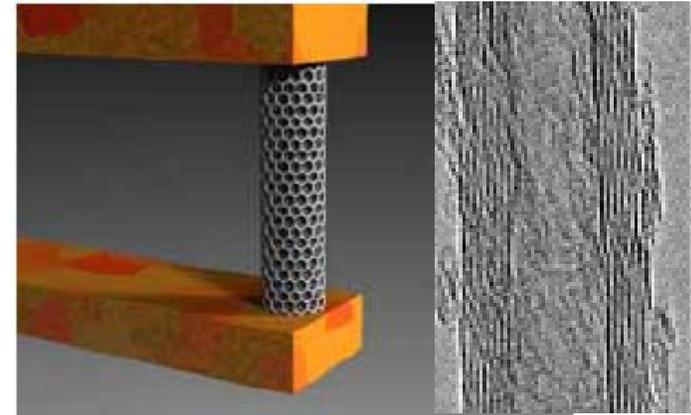


Fujitsu, Samsung



Nihei *et al.* Jpn. J. Apl. Phys. **44**, 1626 (2005)

Infineon

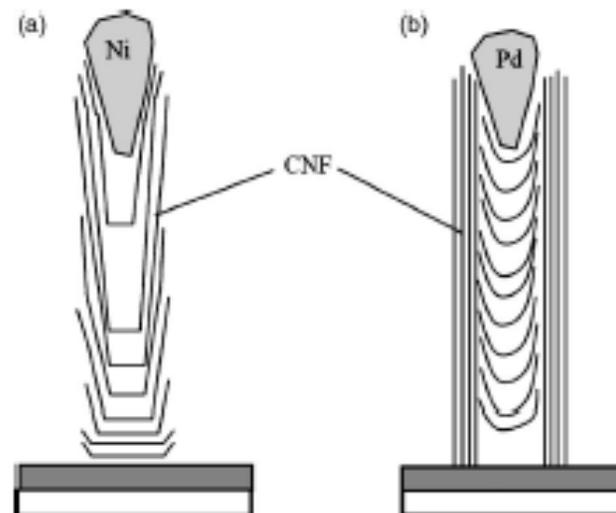
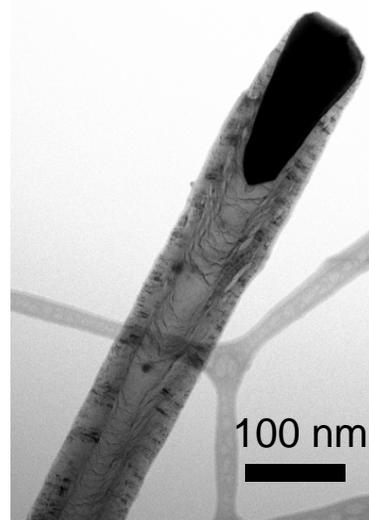
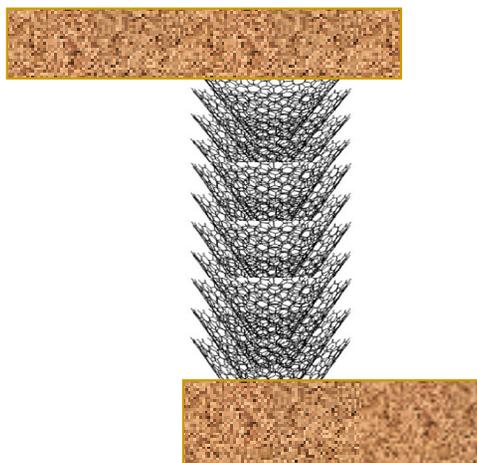


Kreupl *et al.* IEDM 2004

SCU & NASA

Ominami *et al.* Appl. Phys. Lett **87**, 233105 (2005)

Ngo *et al.* Elec. Dev. Lett **27**, 221 (2006)





Institute	Fujitsu	Samsung	Infineon	SCU & NASA
Material	MWNT bundles	MWNT bundles	Single MWNT	Single CNF
Fabrication process				
Via diameter [nm]	2000	700	20	50
Via height [nm]	350	1000	150-200	4000
R [Ω /via]	0.59	1.2 k	7.8 k	9 k (Pd), 13k (Ni)
Resistivity [$\Omega \cdot \text{cm}$]	2.1×10^{-3}	4.6×10^{-2}	1.4×10^{-3}	4.4×10^{-4}
Max. J [$\text{A}/\text{cm}^2/\text{via}$]	$> 2 \times 10^6$	---	$> 5 \times 10^8$	$> 1 \times 10^7$
Reference	Nihei <i>et al.</i> Jpn. J. Apl. Phys. 44, 1626 (2005)	Choi <i>et al.</i> IEEE NANO 2006	Kreupl <i>et al.</i> in IEDM 2004	Ngo <i>et al.</i> IEEE Electron Device Lett. 27, 221 (2006)



CNFs for Thermal Interface Materials (TIM)

Collaborators: B. A. Cruden, J. Li, A. Cassell, M. Meyyappan
Center for Advanced Aerospace Materials and Devices,
NASA Ames Research Center, Moffett Field, CA



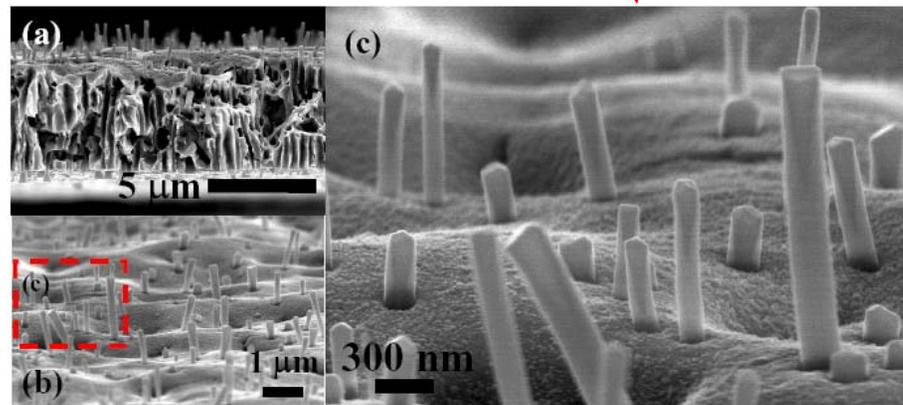
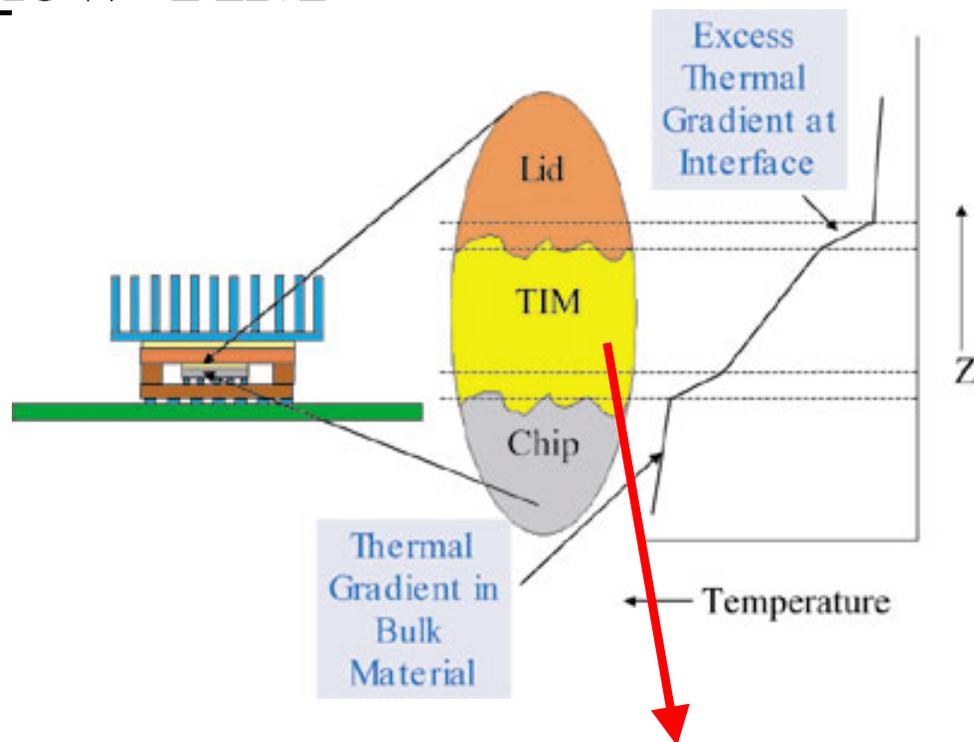
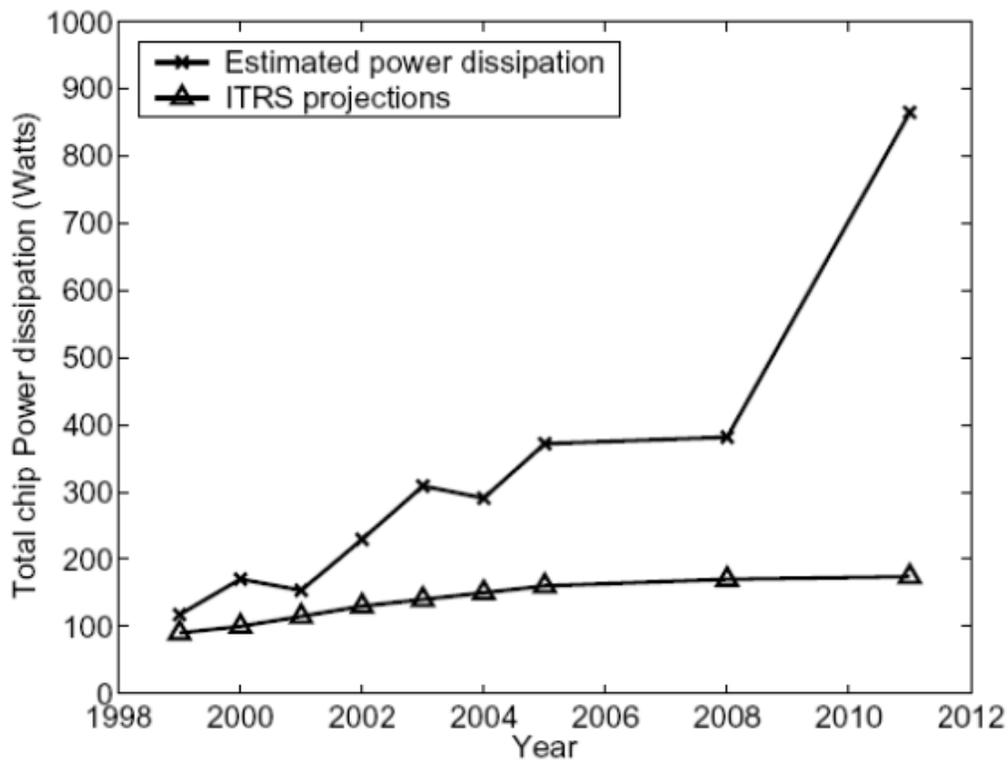
Collaborators: Y. Zhang
Nanoconduction Inc., Sunnyvale, CA





Need for new TIM

G. Chandra et al., IITC 2002

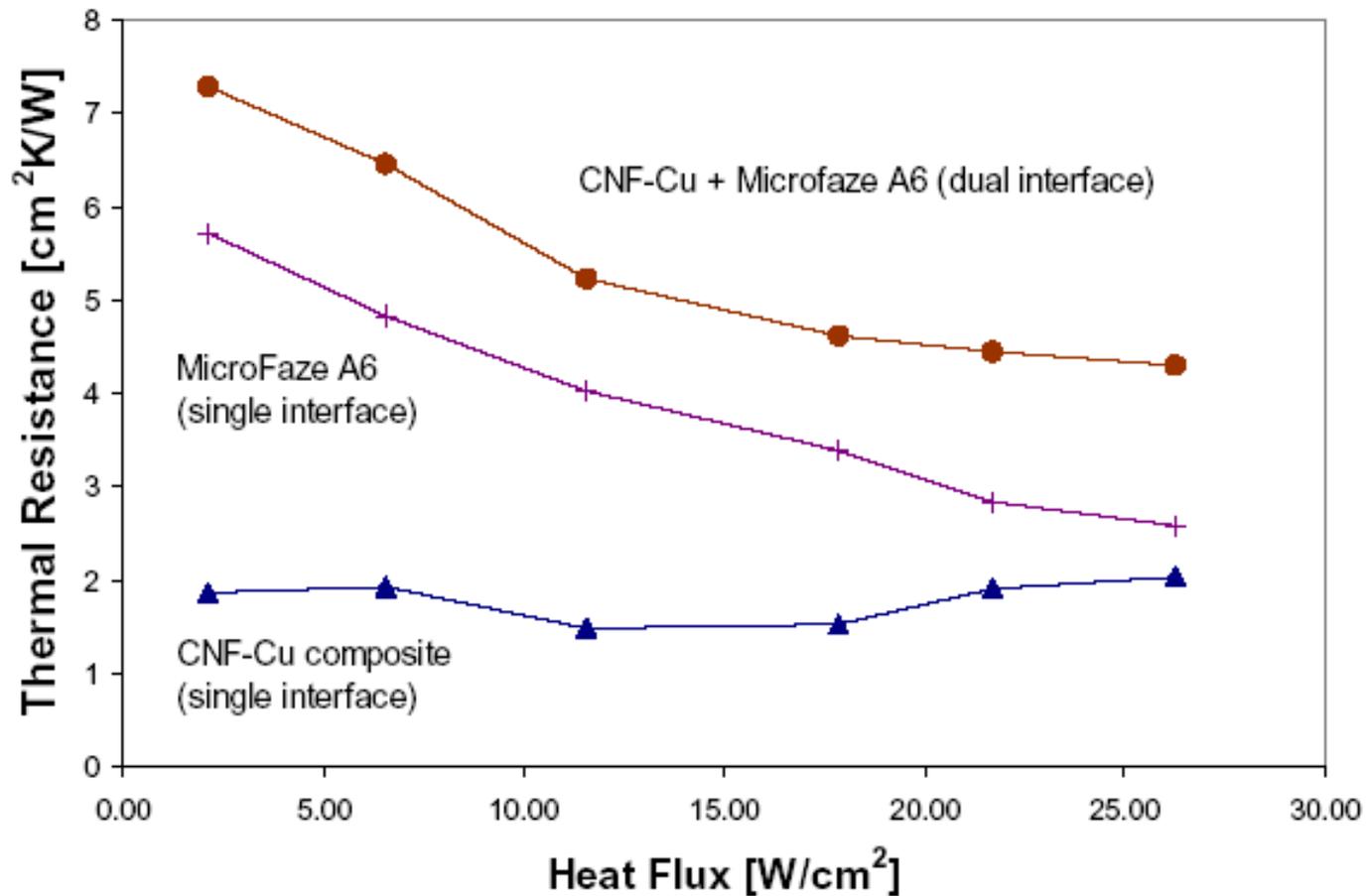


Ngo et al., *Nano Lett.* **4**, 2403 (2004)

Ngo et al., *Proc. ICCE-14* (2006)



Thermal Resistance of CNF-Cu Composite: Power-cycling of CNF-Cu TIM

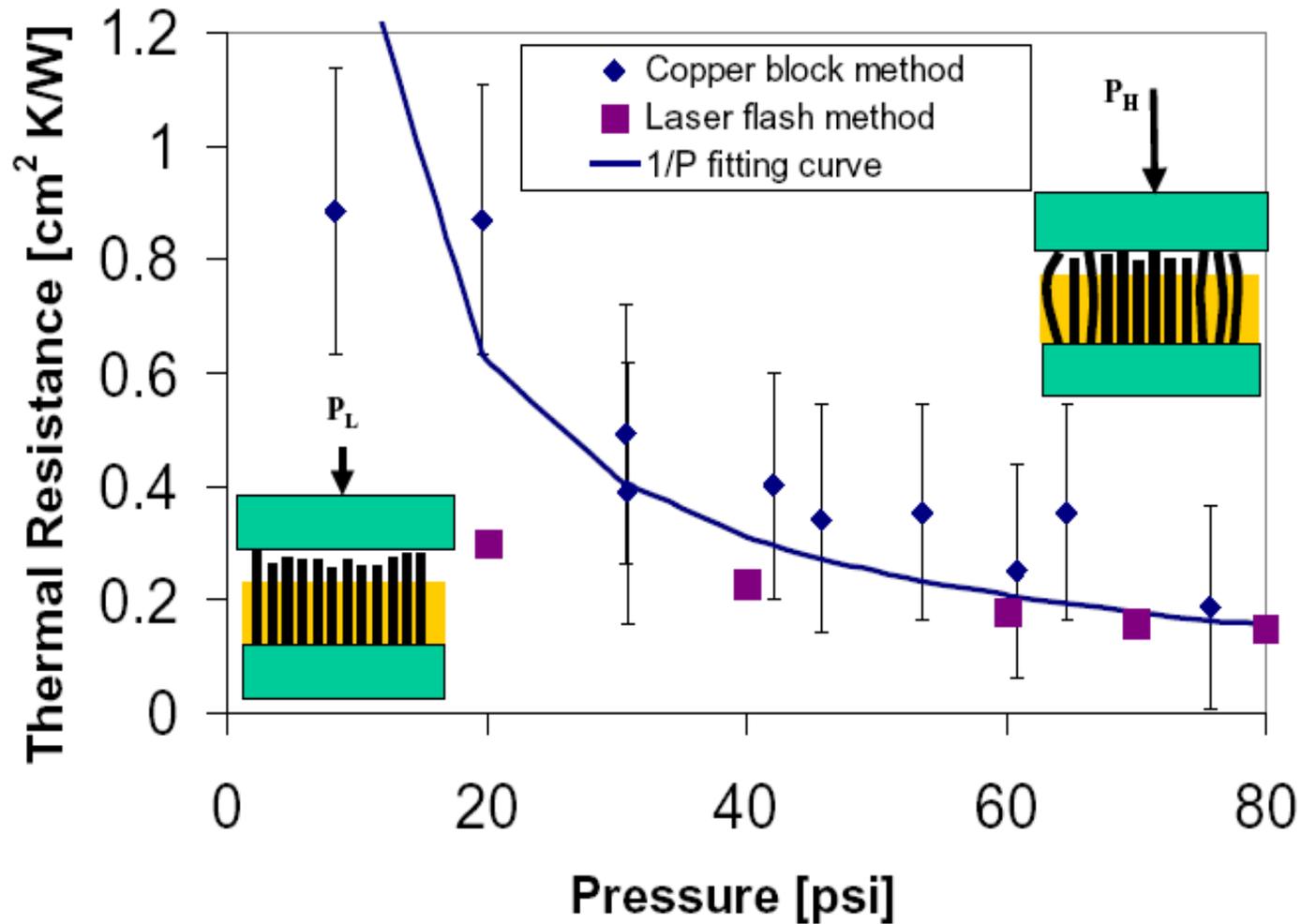


Ngo et al., *Nano Lett.* **4**, 2403 (2004)



Thermal Resistance of CNF-Cu Composite:

Pressure-dependence of CNF-Cu TIM





Continuing Work

- Design and fabrication of new CNF interconnect test structures
- Additional via reliability measurements at high temperature
- Optimization of CNF-Cu TIM for improved thermal resistance
- Electrothermal modeling of thermal effects on electrical characteristics of carbon nanodevices



Thank You!

