Optical and Electrical Characterization of Transparent, Conductive (Separated) Carbon Nanotube Films

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Acknowledgements

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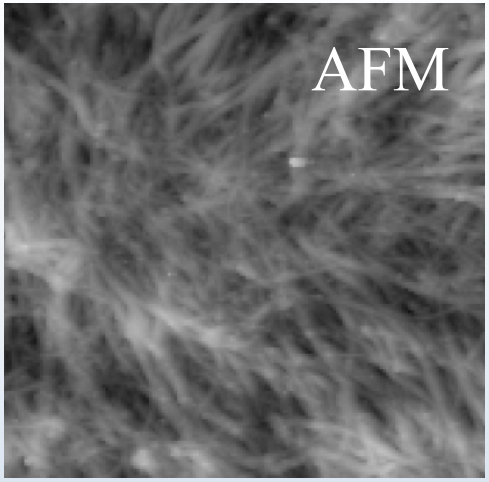
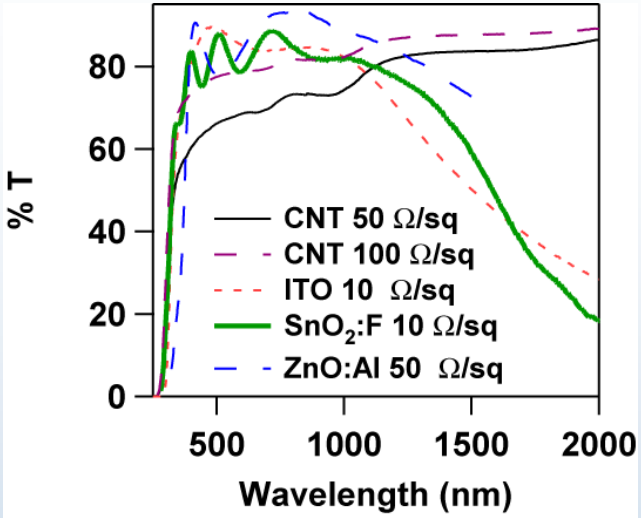
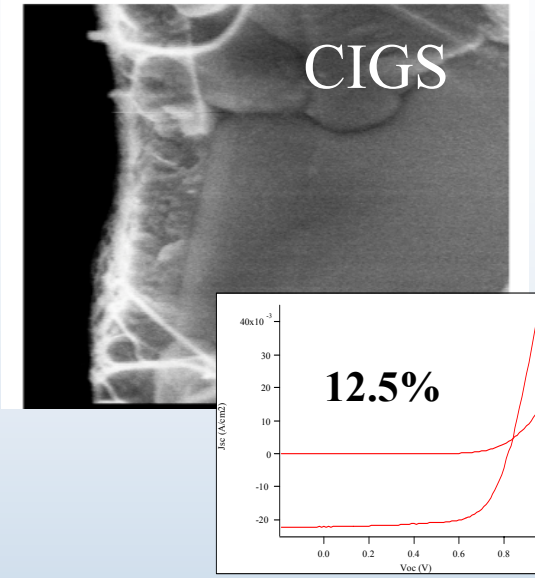
Nanotube Networks as Alternatives to Traditional TCOs







- Good, not great, T and R_S
- Thermally and mechanically stable
- Indium supply
- Spray/print capability

Barnes, APL 2007

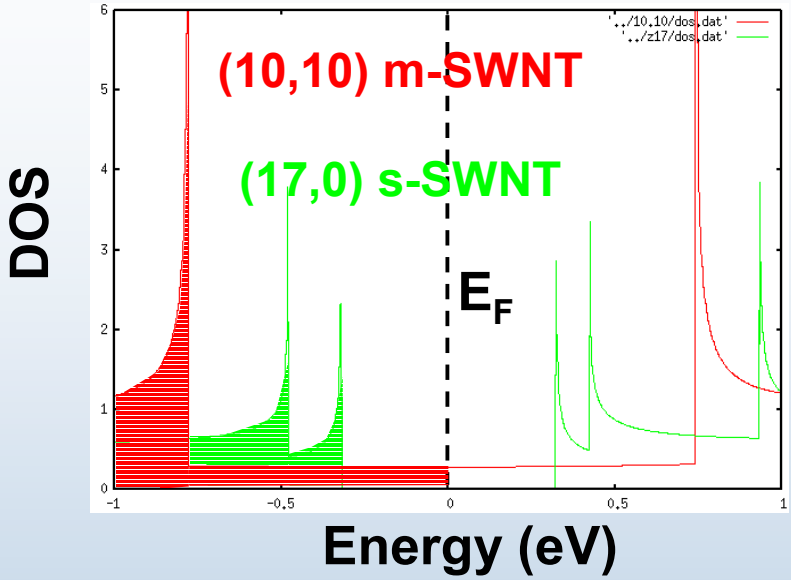
van de Lagemaat, APL 2006

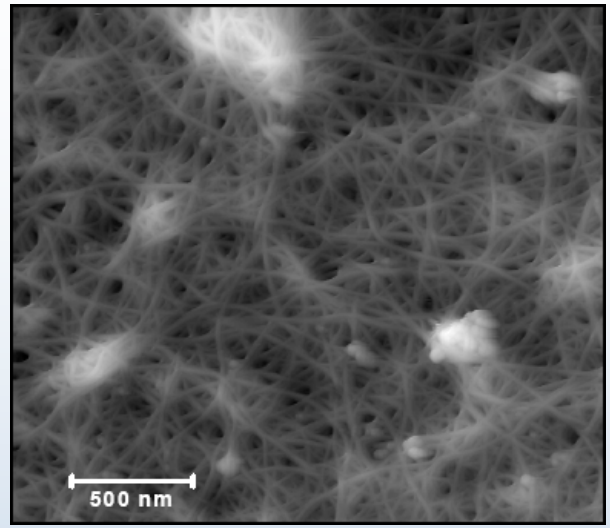
Contreras, J.P.C.B. 2007

Type	η	Ref η	Replaced layer(s)
CIGS	13%	17%	*n*-ZnO
CdTe*	12.4%	13.9%	ITO back contact
OPV	2.5%	~3%	ITO
OPV	1.4%	n/a	ITO/PEDOT

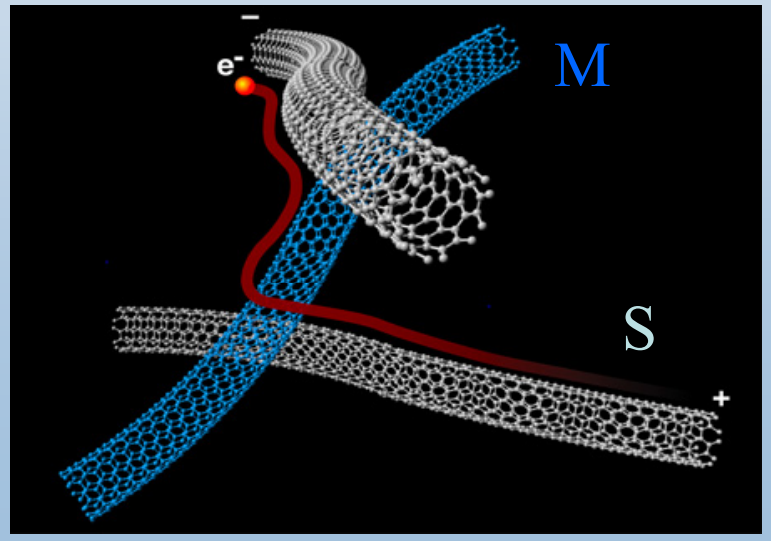
Effect of SWNT Polydispersity on NT-NT interfaces

Intrinsic Conductivity of s- and m-SWNTs?



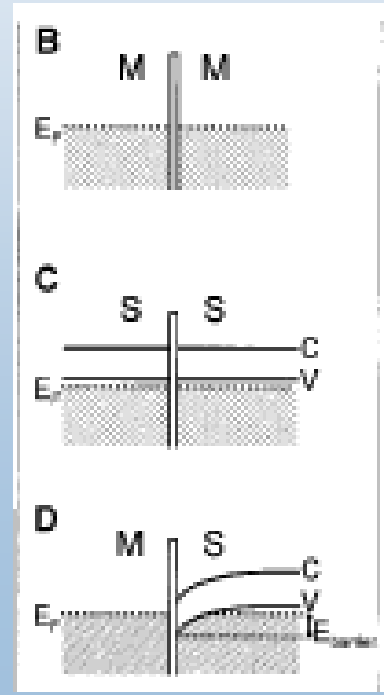


Transport through NT-NT junctions!



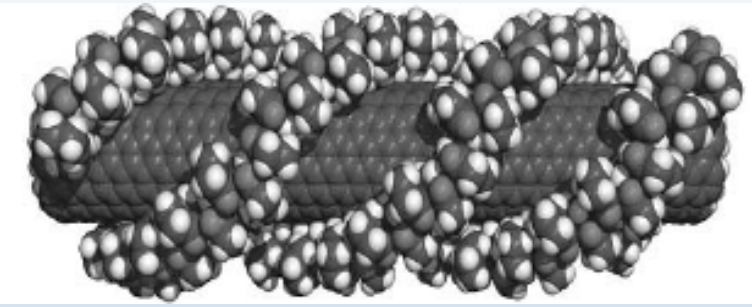
Shottky barriers

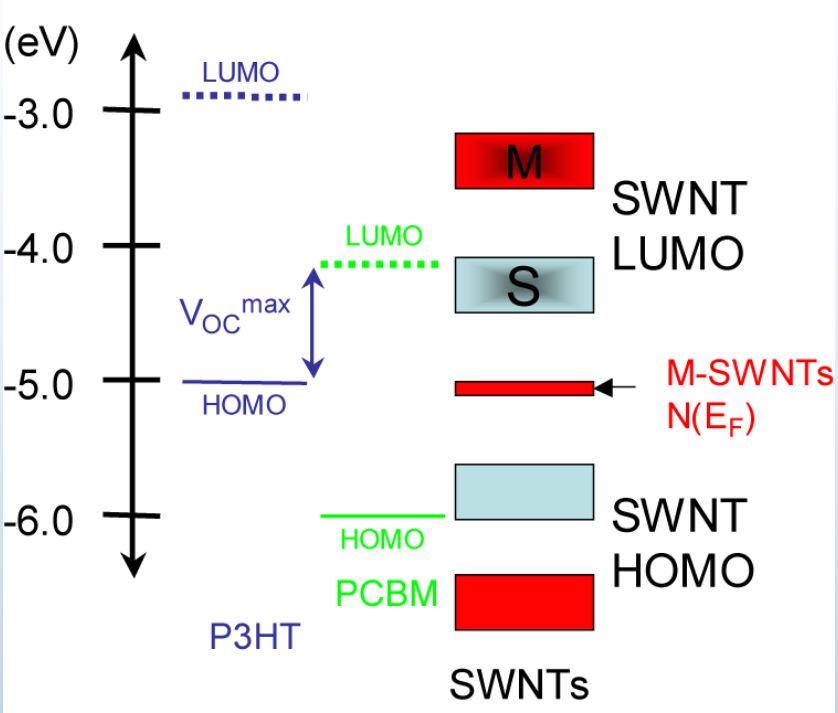
Crossed Nanotube Junctions
M. S. Fuhrer, *et al.*
Science **288**, 494 (2000);
DOI: 10.1126/science.288.5465.494



Effect of SWNT Polydispersity on heterojunctions

SWNT-polymer





- Is charge transfer/exciton dissociation favored at interfaces with m-SWNTs or s-SWNTs?
- How does N_{EF} of m-SWNTs control charge transfer/transport?
- Can we optimize devices through strategic separations?

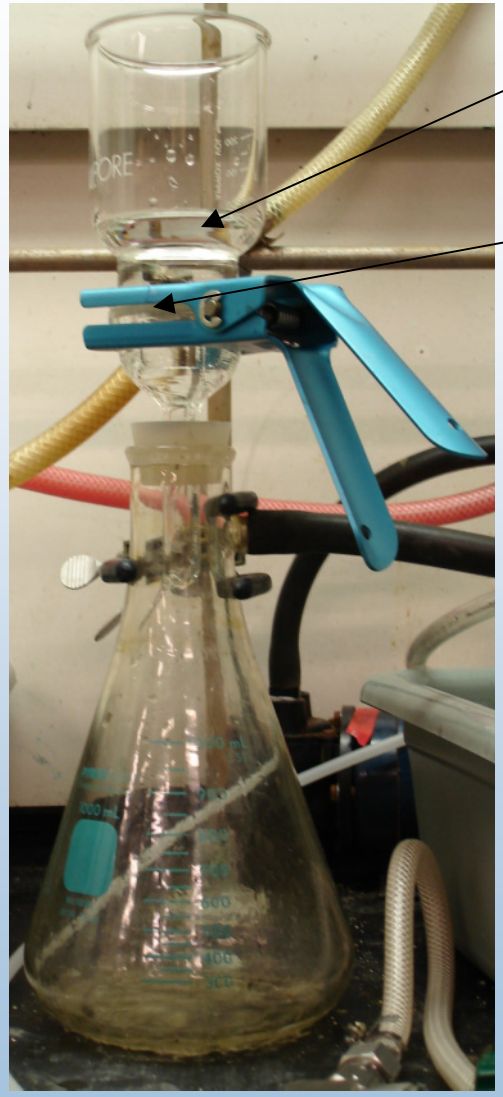
Known problems with SWNT conductive electrodes

- Visible Transmission and Conductivity are controlled by dopants and are slightly lower than traditional TCOs
- Resistance irreversibly increases above room temperature – problematic for device fabrication and cell reliability

Can Nanotube Separations Address These Problems?

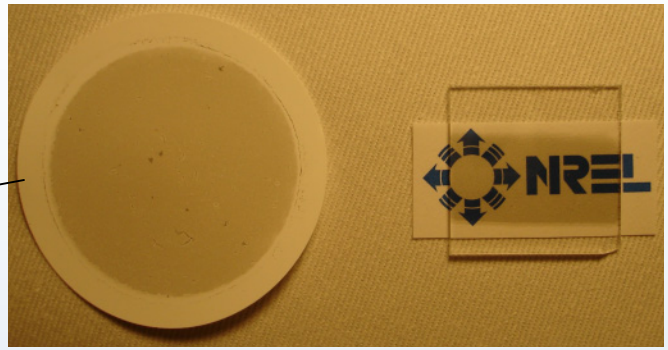
- How does metal/semi ratio affect transmission and conductivity of SWNT films?
- Do dopants affect metals and semiconductors similarly?
- Can separated films provide better thermal stability?

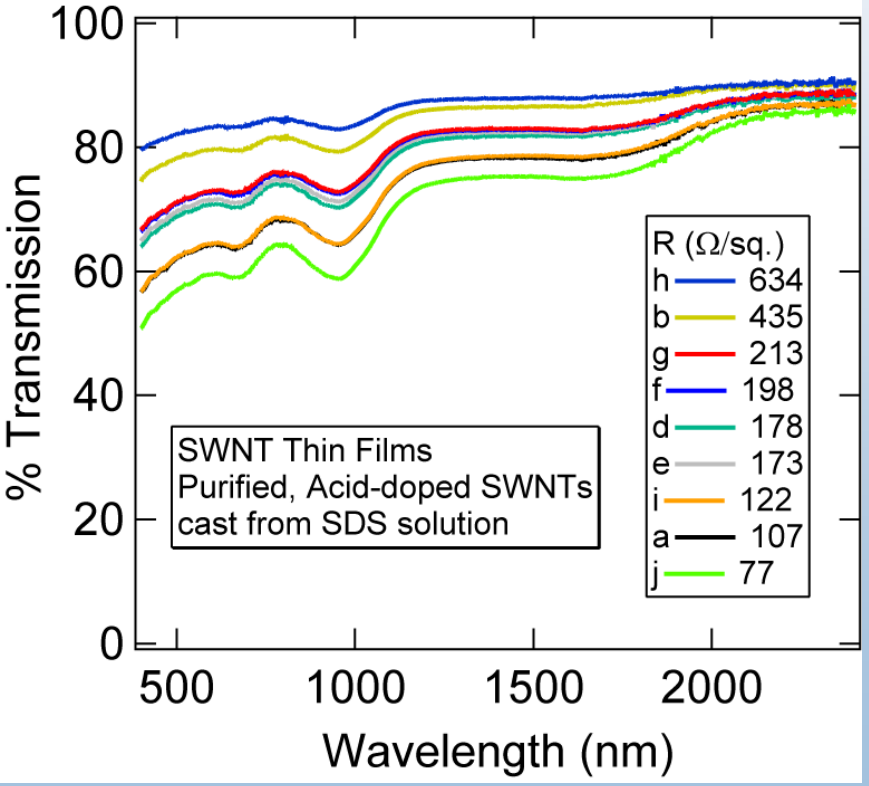
SWNT Films by Solution Filtration



SWNT soln.

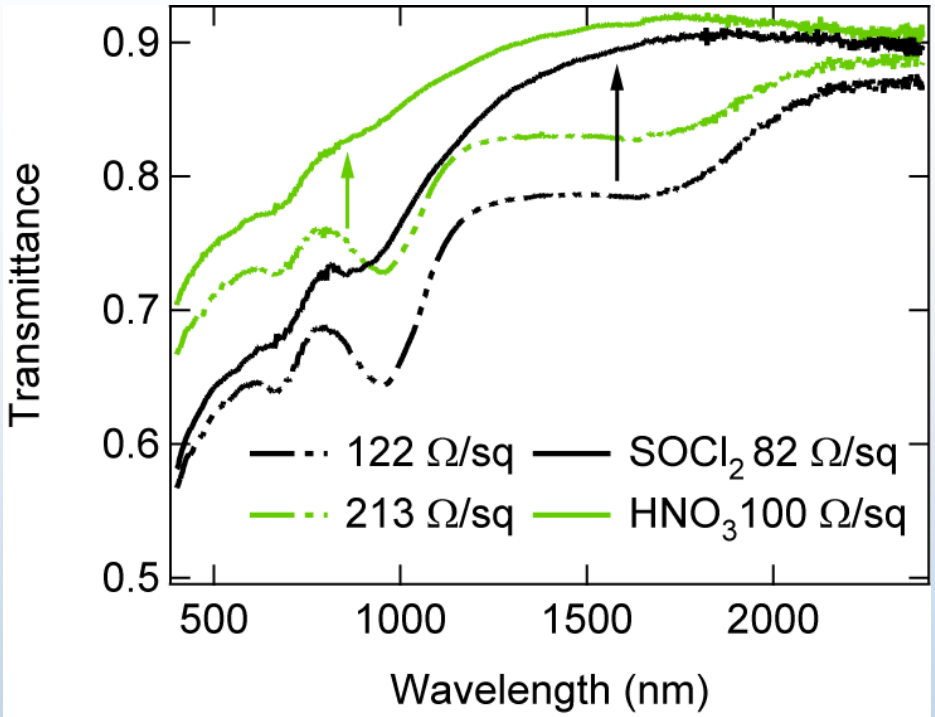
MCE membrane





Wu, *Science*. **305**, 1274 (2004)

Controlling T and R with Doping

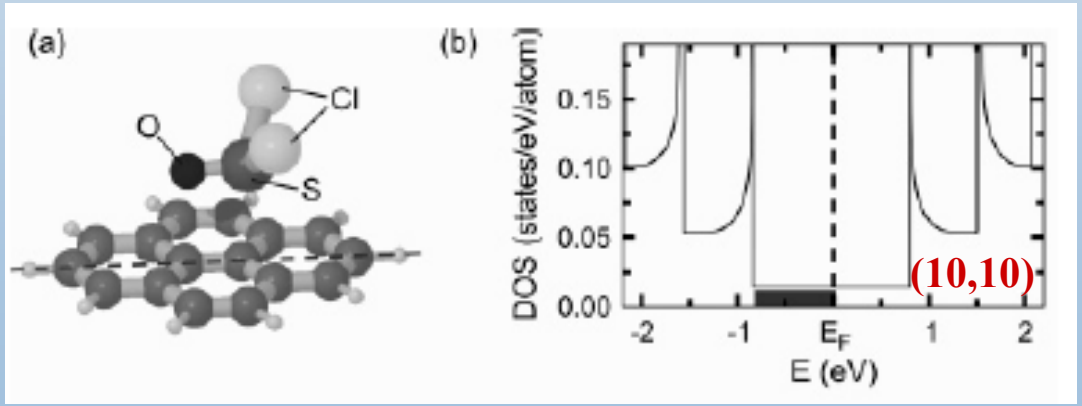


	PLV +HNO_3	PLV +H_2SO_4
E_F (eV) (Seebeck)	0.33	0.46
E_F (eV) (Raman)		
E_F (eV) (Reflectivity)	0.32–0.51	0.51–0.62

Acid Doping

P.R.B., **71**, 205423 (2005)

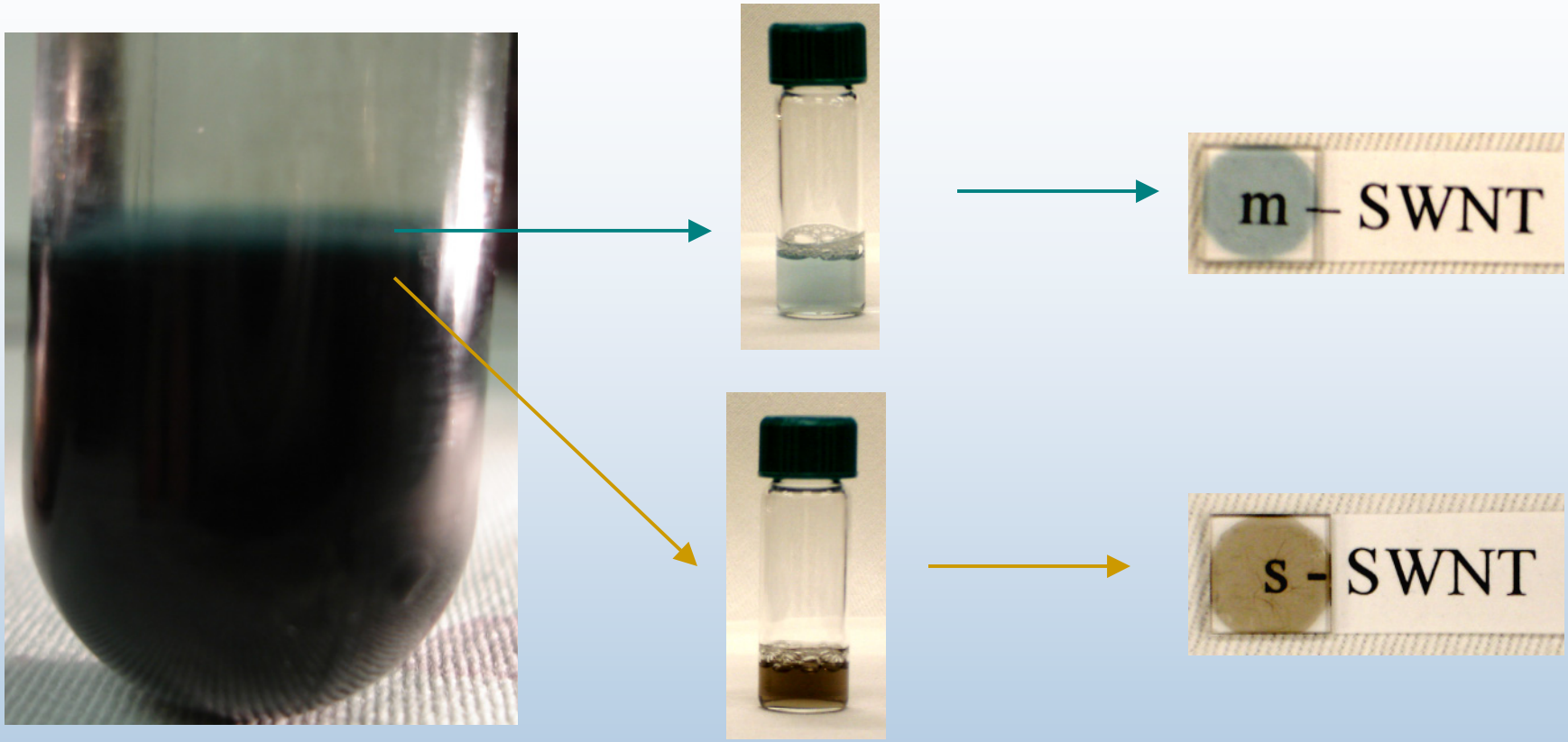
- Acceptor dopants lower E_F, bleach excitonic transitions, and lower R_S
- $SOCl_2$ predicted to chemisorb, lower E_F into VB for s-SWNTs and m-SWNTs
- Thermal Stability?



Thionyl Chloride

J.A.C.S., **127**, 5125 (2005)

Separating Metallic and Semiconducting SWNTs by Density Gradient Centrifugation



Arnold, *Nature Nanotech*. **1**, 60 (2006)

Conditions:	•1 mg/ml raw laser SWNTs		•tip sonication, 40%/40 min
	•no centrifuge	•3:2 SDS:SC (2%)	• 1 ml SWNTs
	•Ti70 rotor	•47,000 rpm (225,000 g)	

Some Figures of Merit for analyzing trends

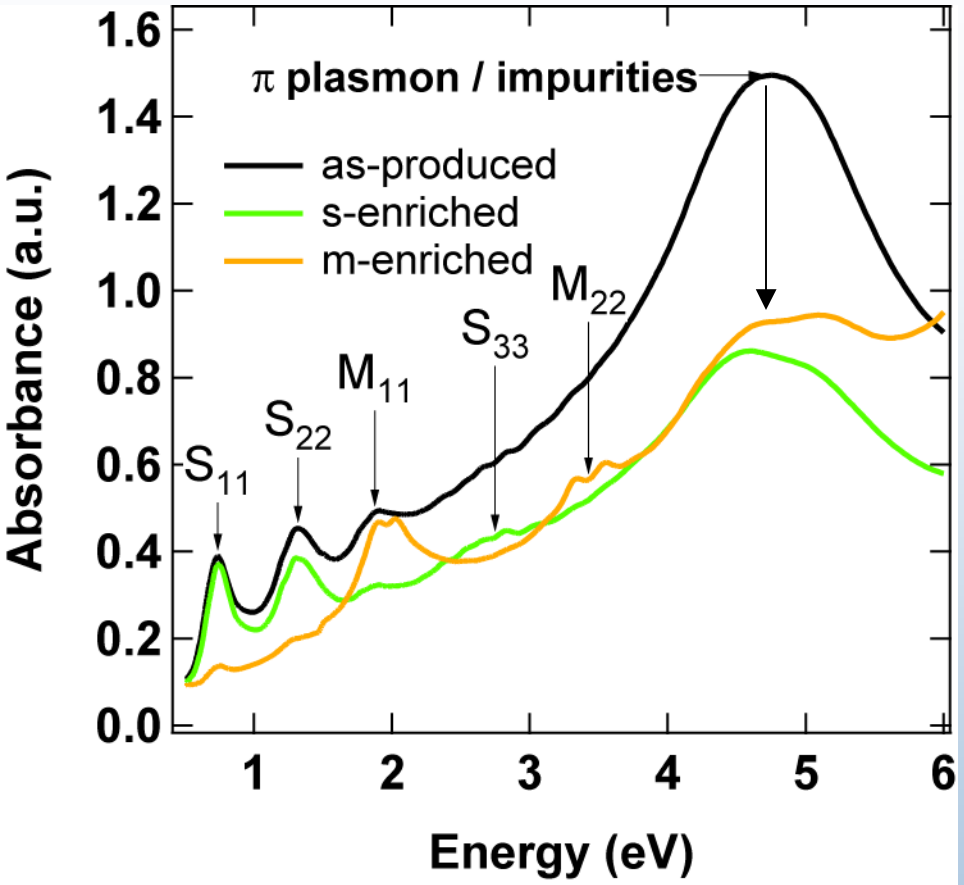
I. Metal and Semiconductor Ratios
- Integrated areas in Absorbance spectra
- Thermoelectric responsivity (NIST)

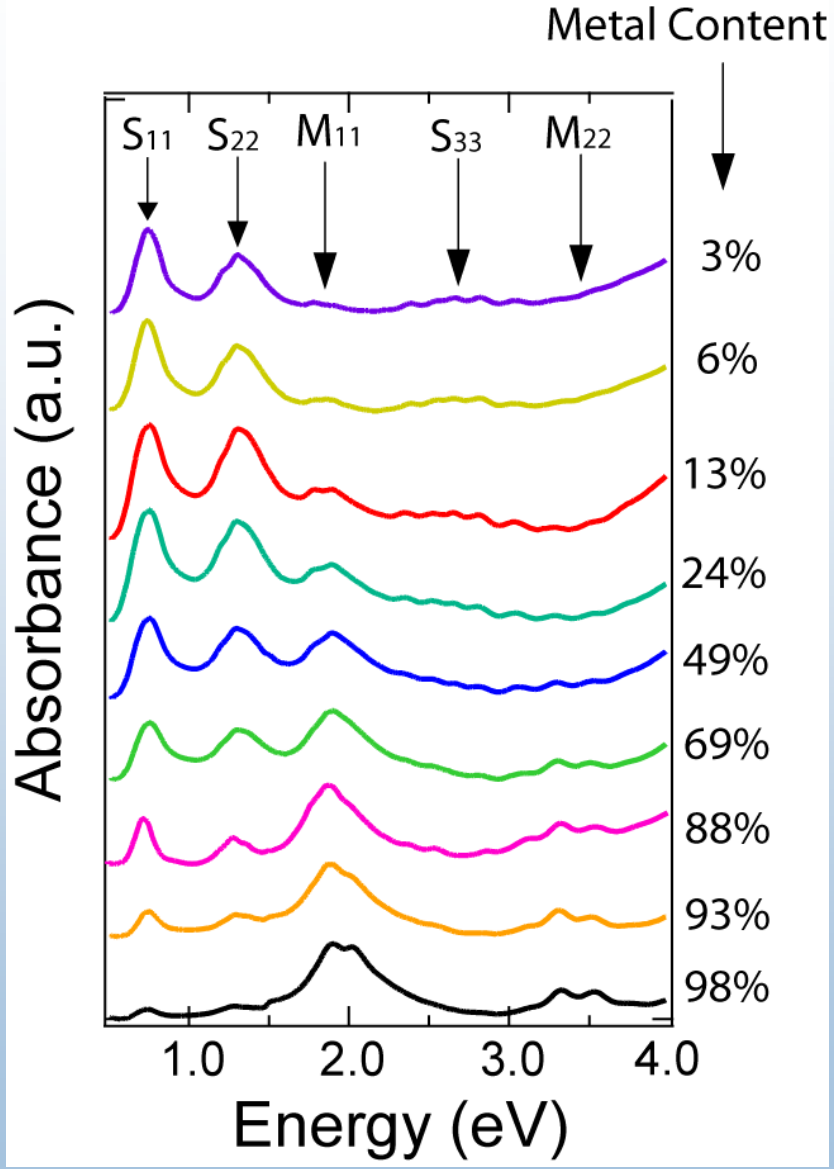
II. Total SWNT concentrations
- Film thickness: AFM – several issues
  - Large RMS roughness (often comparable to film thickness)
  - Film morphology, packing changes with M/S ratio or SWNT treatments (e.g. purification)
- Total (weighted) integrated area (α total density of C)

III. Electrical Properties
- Sheet resistance: four-point probe, Hall, THz
- Length: ???

IV. T/R is ultimate F.O.M. for conductive electrodes – needs to be as high as possible

Absorbance Spectra of Separated Films

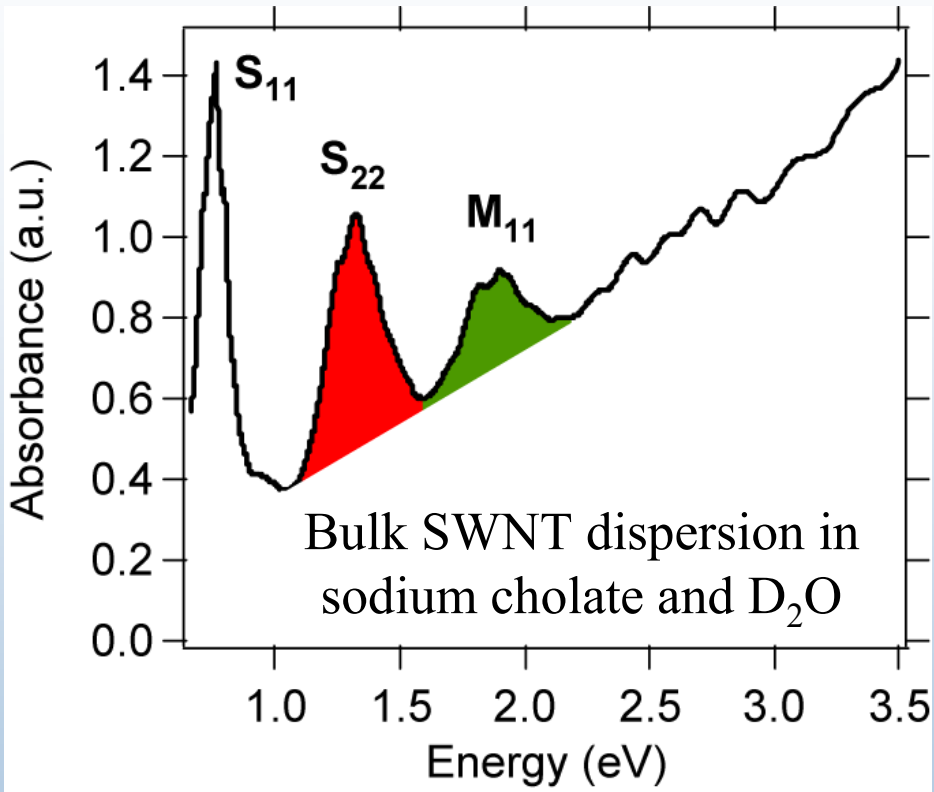




T in visible enhanced by lowering of high energy (~4.8 eV) absorbance

High E peak subtracted

Optical Characterization of Metal/Semi Ratio (and thickness)



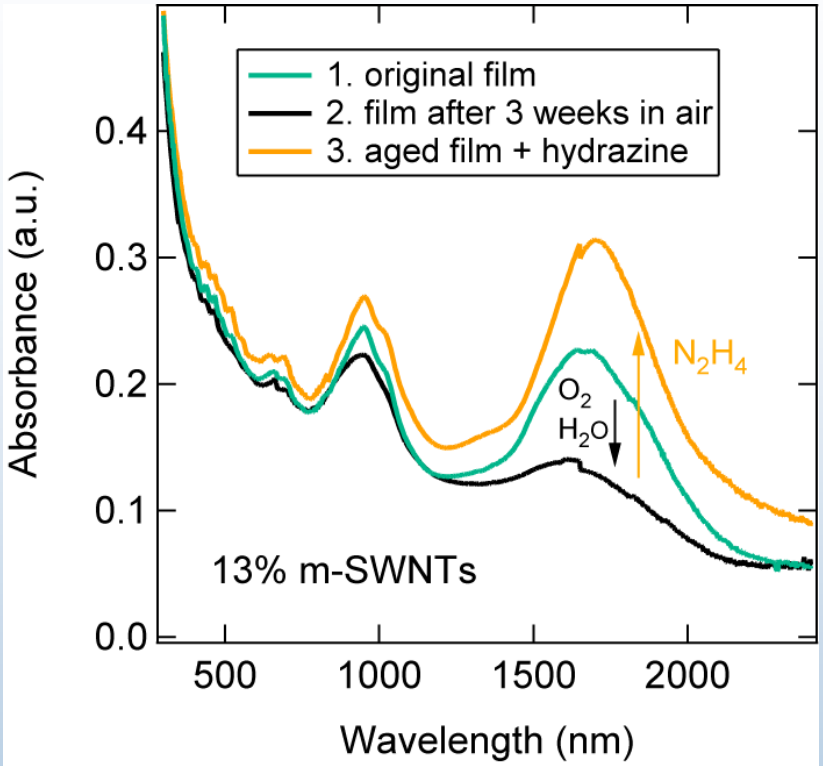
- Integrate area underneath S_{22} and M_{11} envelopes
- Beer's Law
  - $OD_{M11} = \varepsilon_{M11} \cdot b \cdot c_M$
  - $OD_{S22} = \varepsilon_{S22} \cdot b \cdot c_S$
- $\Rightarrow \varepsilon_{S22} \approx 1.155 \cdot \varepsilon_{M11}$

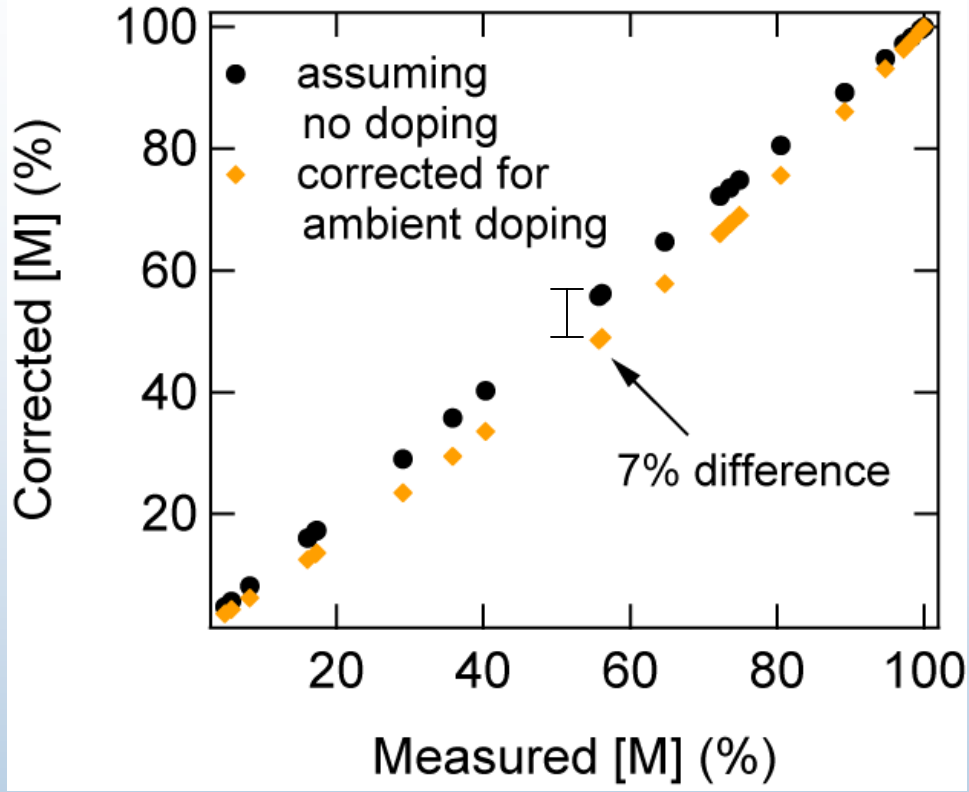
**AFM film thickness correlated with integrated OD $\Rightarrow$ optically measured effective thickness

Assumptions:

- 1/3 m-SWNTs and 2/3 s-SWNTs
- No significant change in diameter distribution

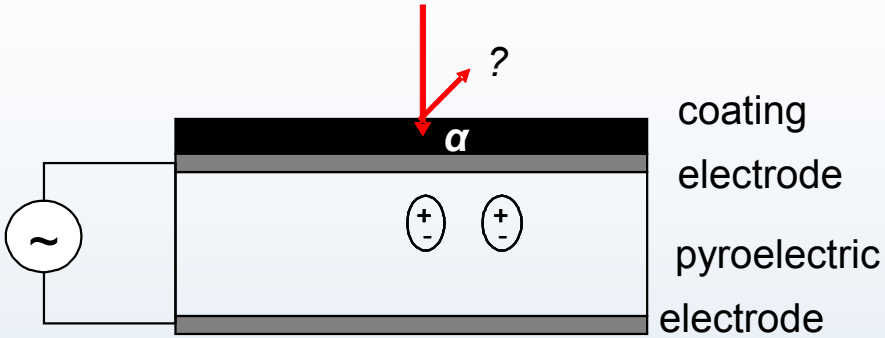
Errors from Unintentional Doping

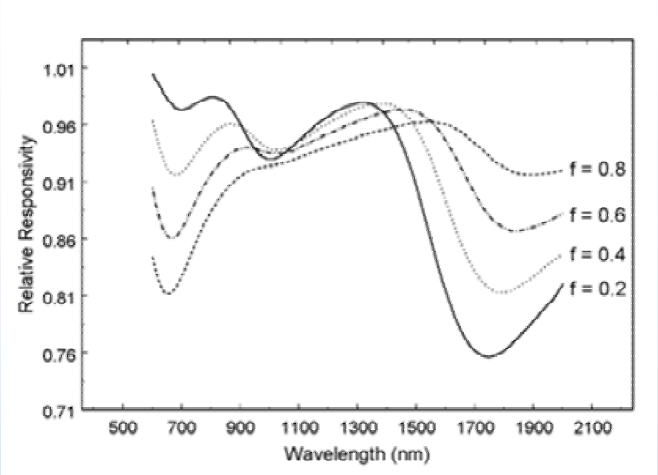




- O_2, H_2O dopes films sitting in air - doping can be reversed by hydrazine
- S-SWNTs (esp. S_{11}) most susceptible $\Rightarrow$ must use S_{22} and must ensure correction for unintentional doping

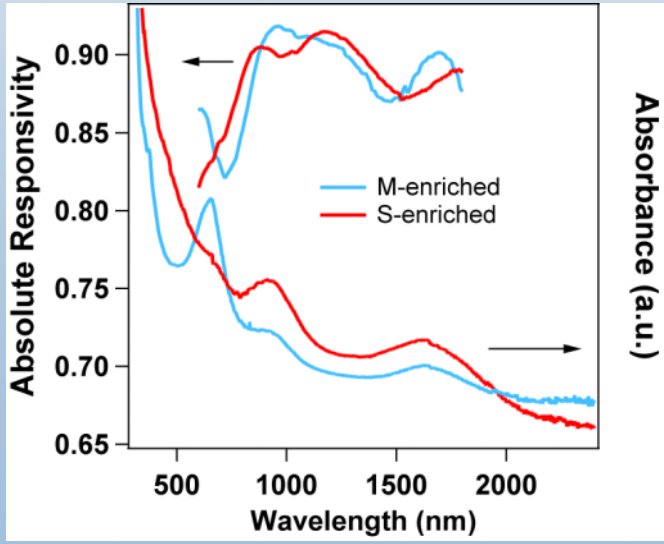
Characterization of metal/semi ratio using a pyroelectric detector (NIST, Boulder)

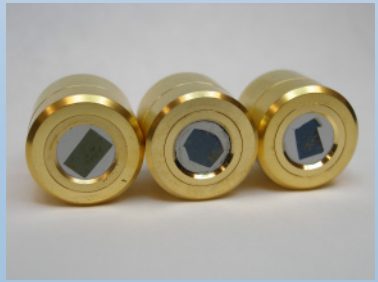




$$f\frac{\varepsilon_m - \varepsilon}{g\varepsilon_m + (1-g)\varepsilon} + (1-f)\frac{\varepsilon_s - \varepsilon}{g\varepsilon_s + (1-g)\varepsilon} = 0$$

Estimate the volume fraction of metallic:semiconducting nanotubes by employing an effective medium approximation





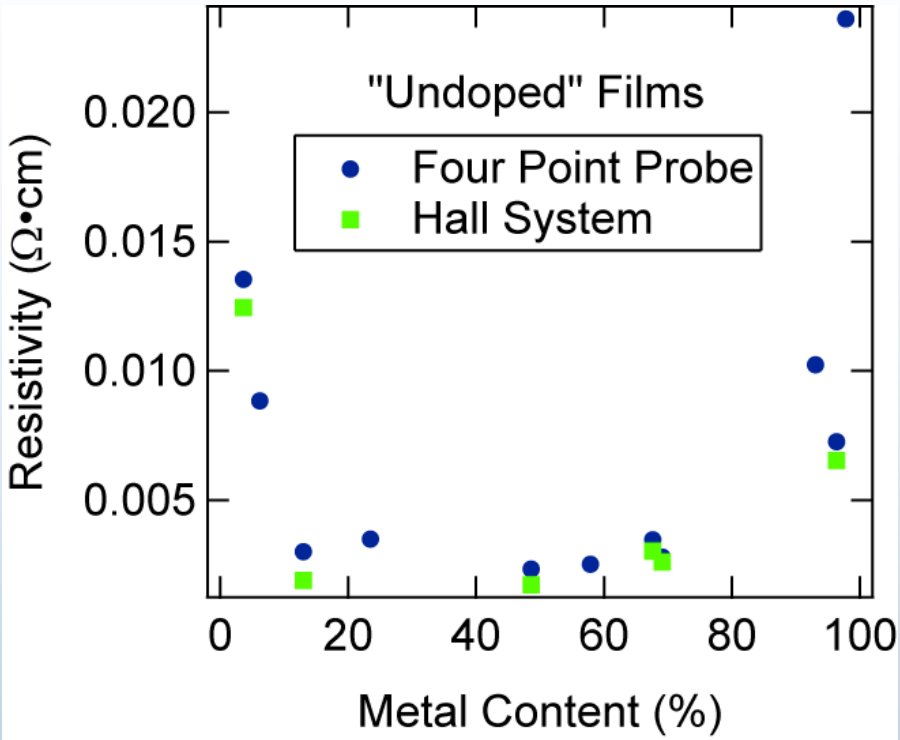
Lehman, Engtrakul, Gennett, and Dillon Appl. Optics (2005) 44 483

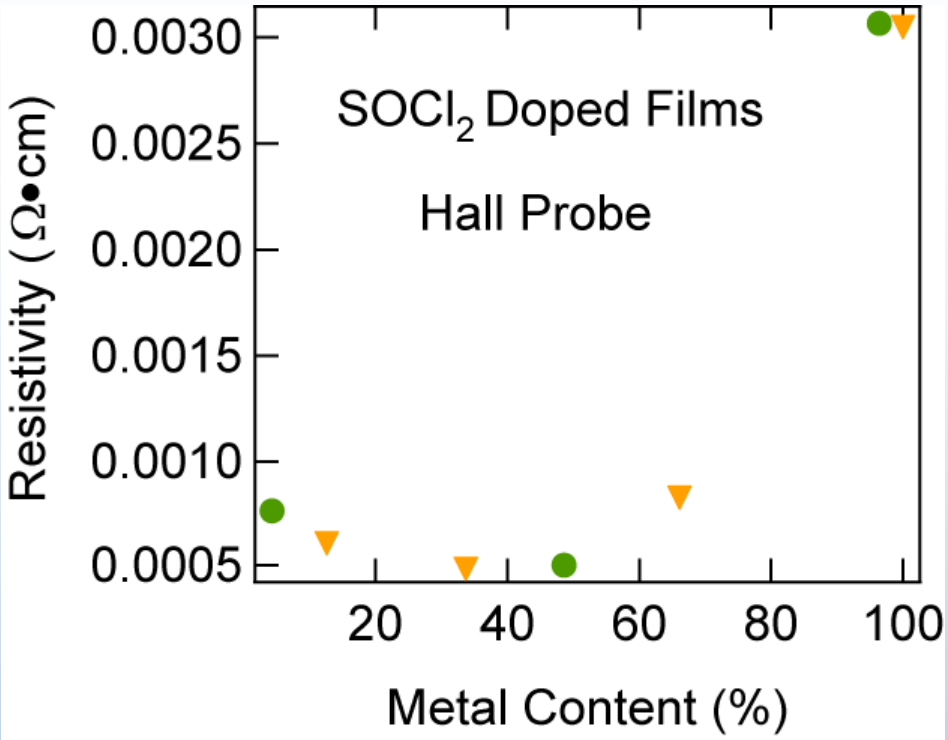
Hurst, Lehman, Dillon and Blackburn APL (2005) 88, 143122

Conductivity

I. Metal / Semiconductor Ratio

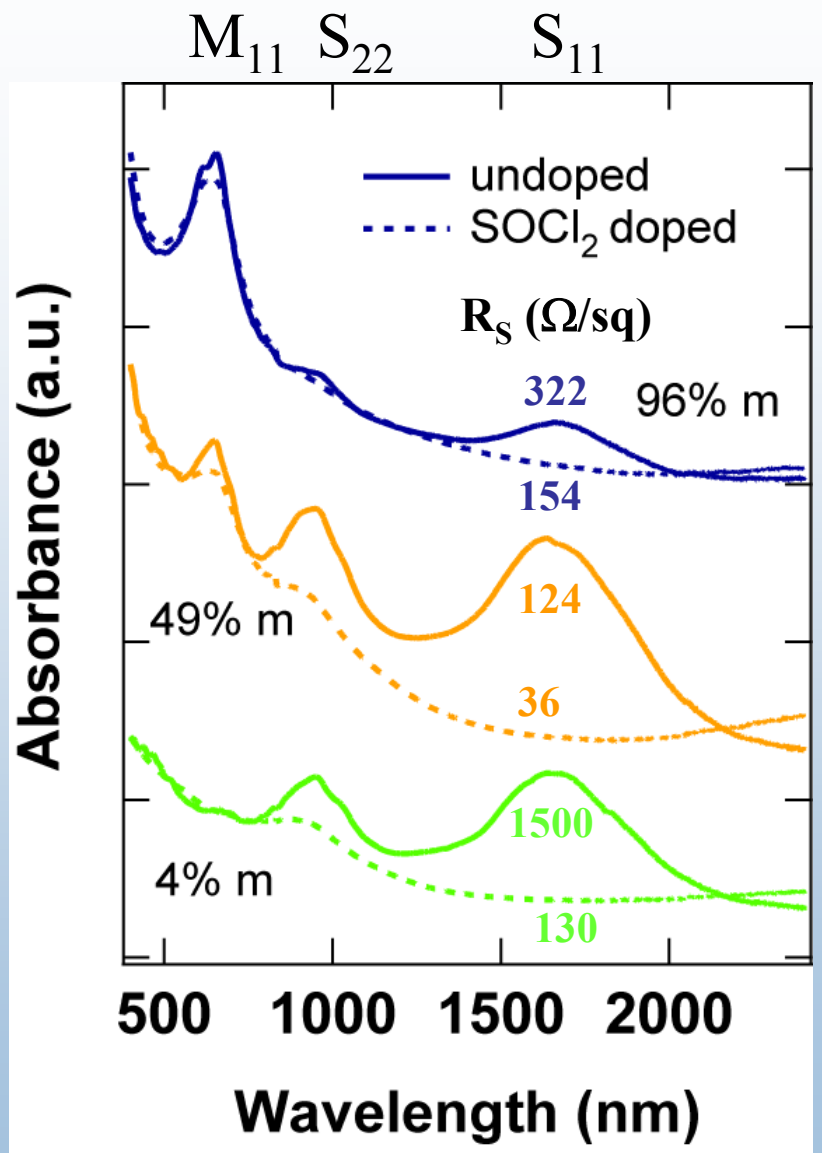
Strong Dependence of R on M/S Ratio and Doping



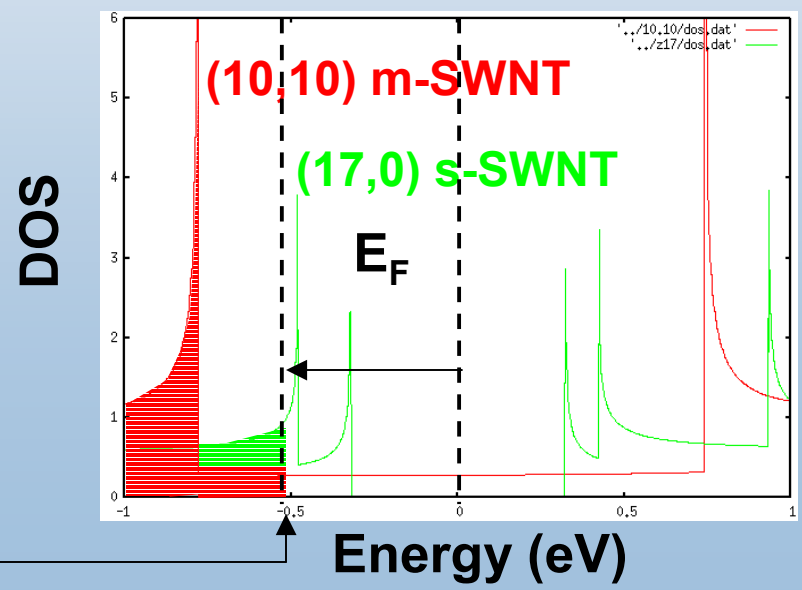


- Highly enriched "undoped" s- or m-SWNT films have highest R
- Doping with $SOCl_2$ lowers resistivity for both m- and s-enriched
  - $\Delta R(\%)$ significantly higher for s-enriched
  - Doped s-SWNTs produce most conductive films

Are m- and s-SWNTs both effectively doped?



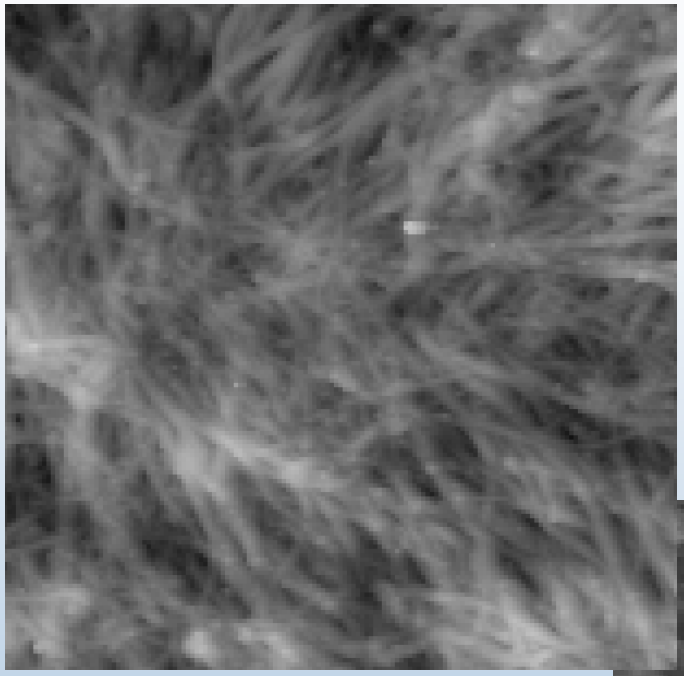
- ΔO.D. (bleaching) of both S_{11} and S_{22}
- M_{11} only slightly bleached
- A spectra allow us to approximate the doped E_F
- ** $N_{EF}(s) > N_{EF}(m)$



Estimated depletion of electrons

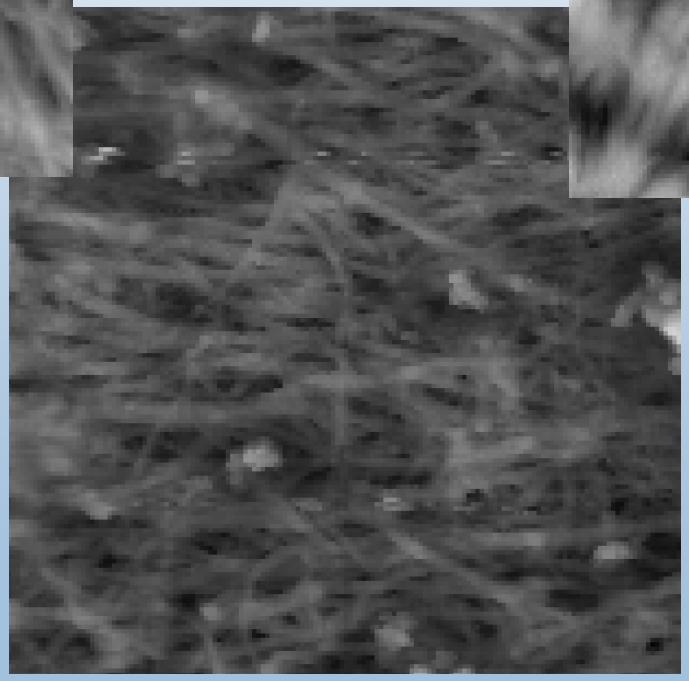
Raw Separations: Film morphology depends on nanotube type

metals & semis

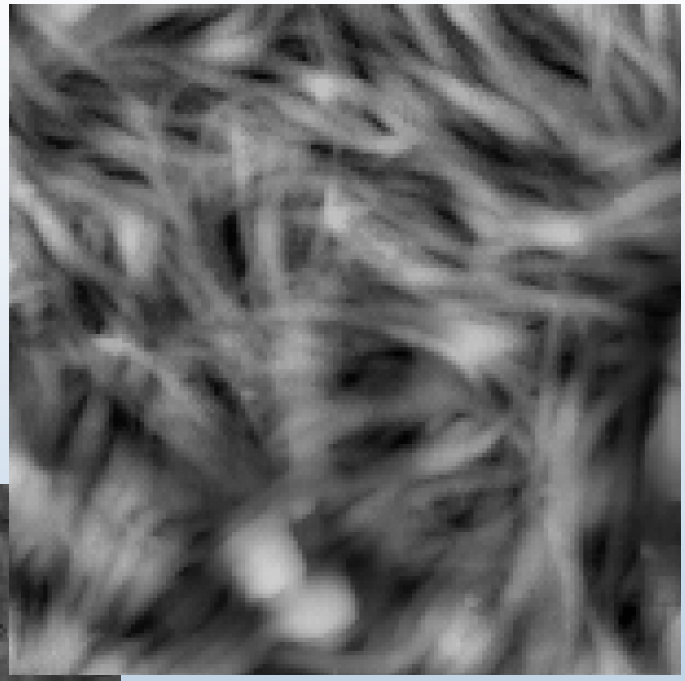


1 μm

95% semis



98% metals



- Tube rebundling depends on physics of interaction
- Effect on electrical properties?

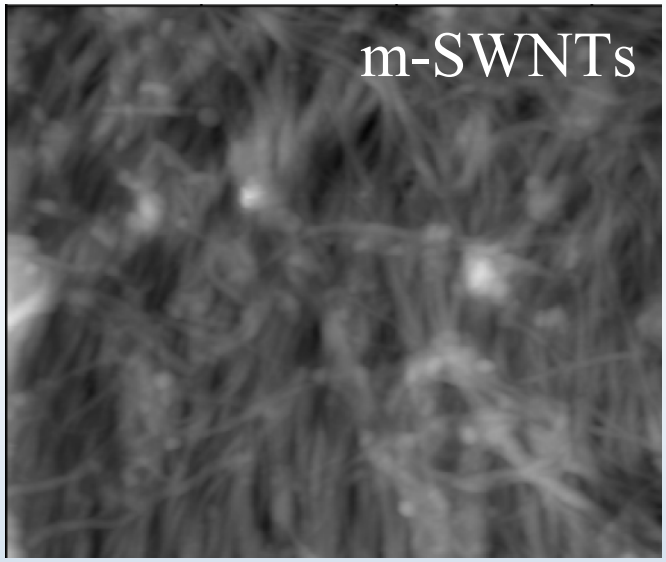
Separation of Purified SWNTs

Conditions

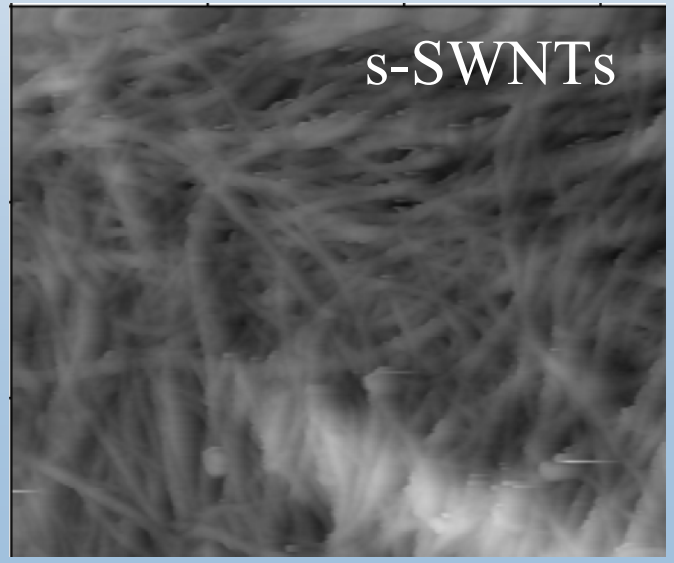
- Laser SWNTs purified with 24 hr. HNO_3 (3 M) reflux
- Non-nanotube C removed with acetone/H_2O/KOH iterations
- ⇒ Thin (~5 μm) buckeypaper doped with residual acid
- Tip sonication: 5 min. at 25%, 13 min. at 40%
- Same density gradient conditions

Hopes

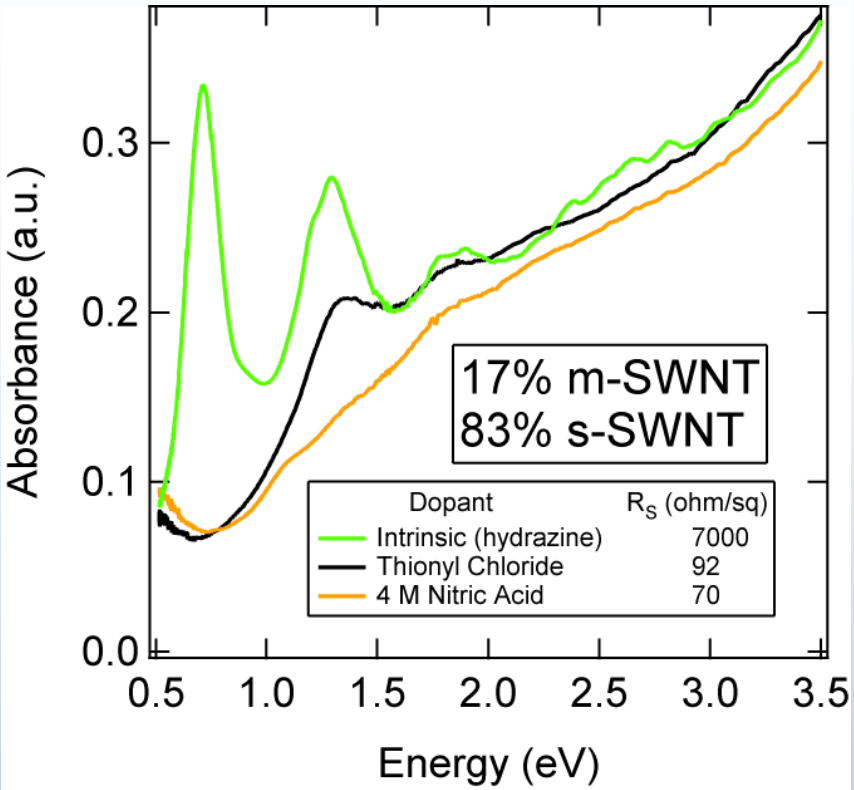
- Surface charge on NTs will affect packing
- Less aggressive sonication will leave NTs longer and less defective

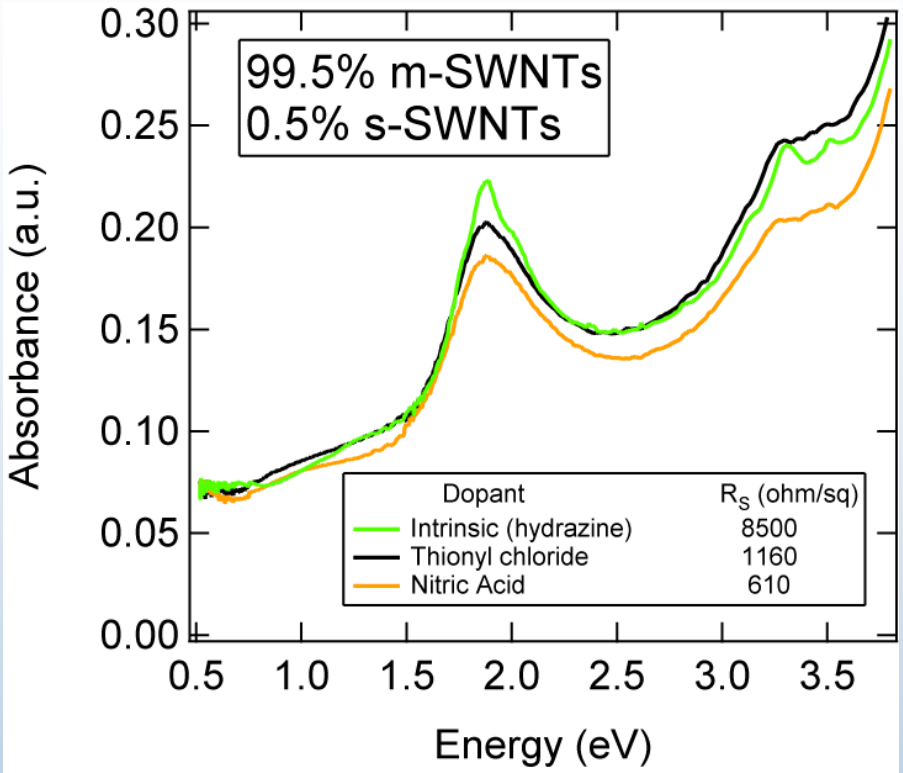


1 μm



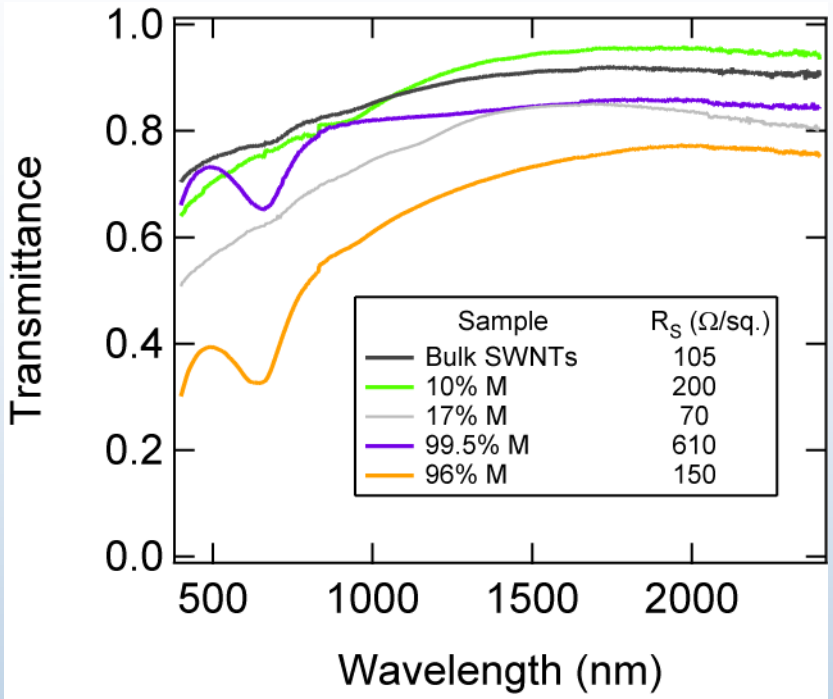
Separation of Purified SWNTs

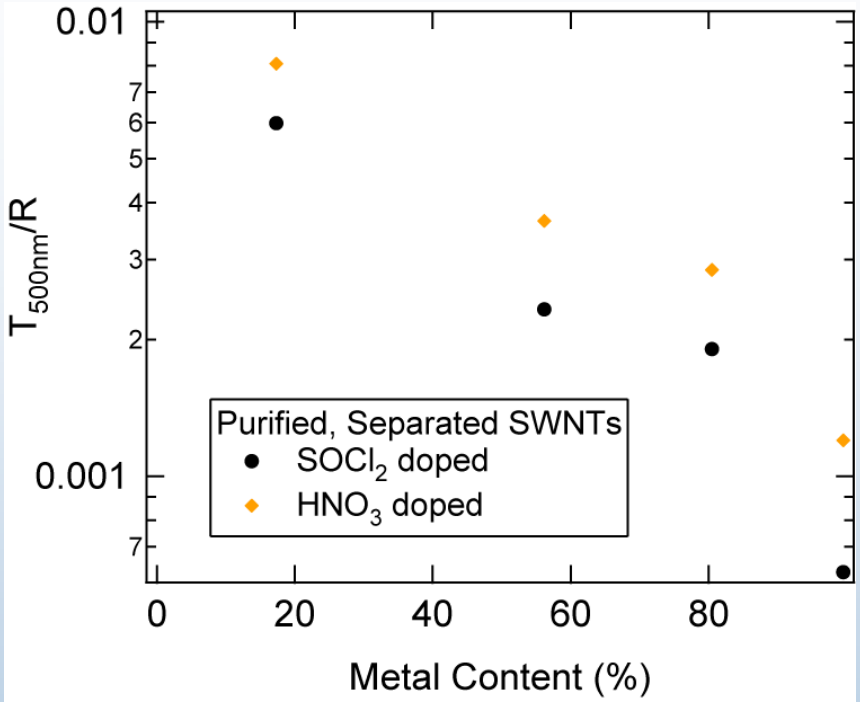




- Purified, separated SWNTs show same trends as raw separations
- Slightly lower R_S compared to more vigorously sonicated raw SWNTs (length, bundling, impurities?)
- Nitric acid found to be most effective dopant, M_{11} still ineffectively bleached
  - Is R_S decrease for m-SWNTs caused by surfactant removal, better contacts?

Ultimate Performance of Separated Transparent Conductive SWNT Films





- T/R figure of merit scales with concentration of degenerately doped s-SWNTs
- Why are m-SWNT films so resistive? Length?
- Our separated samples don't quite match or exceed performance of bulk SWNTs
  - Optimization to remove more non-nanotube impurities (D.G.)
  - Trends suggest improvements should be expected from pure (doped)s-SWNTs

Conductivity

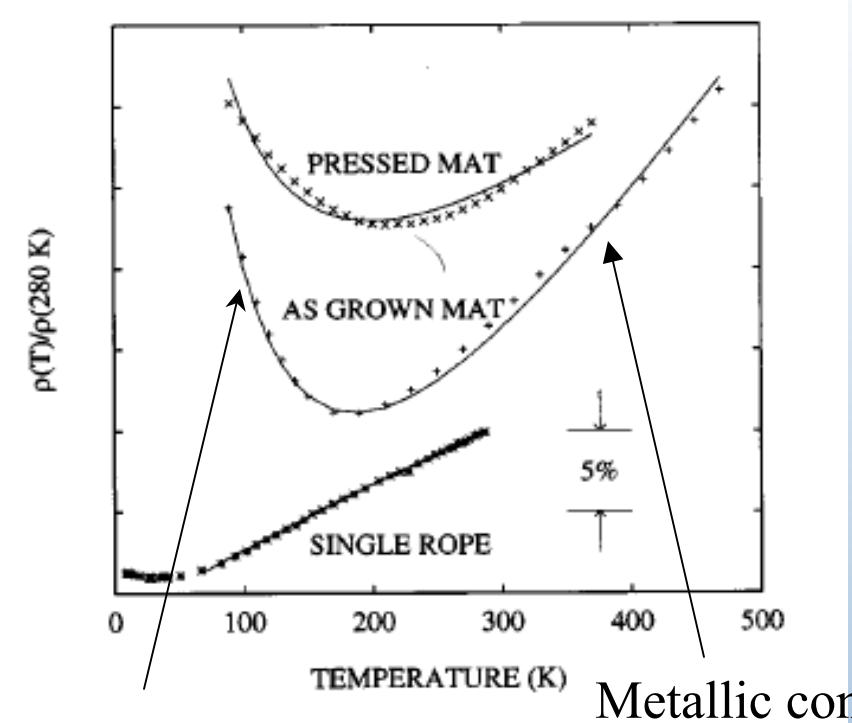
II. Thermal Stability

Temperature Dependence of Resistance

PHYSICAL REVIEW B VOLUME 55, NUMBER 8 15 FEBRUARY 1997-II

Metallic resistivity in crystalline ropes of single-wall carbon nanotubes

J. E. Fischer,[1] H. Dai,[2] A. Thess,[2] R. Lee,[1] N. M. Hanjani,[1] D. L. Dehaas,[1] and R. E. Smalley[2]



"Interrupted Metallic Conduction Model"

-analogous to conducting polymers

$$\rho(T) = \frac{1}{\sigma(T)} = A\exp\left(-\frac{T_m}{T}\right) + \beta\exp\left(\frac{T_b}{T_s + T}\right)$$

Regions of metallic conduction separated by thin barriers ⇒ "semicondcuting" behavior at low T and "metallic" behavior above T_c

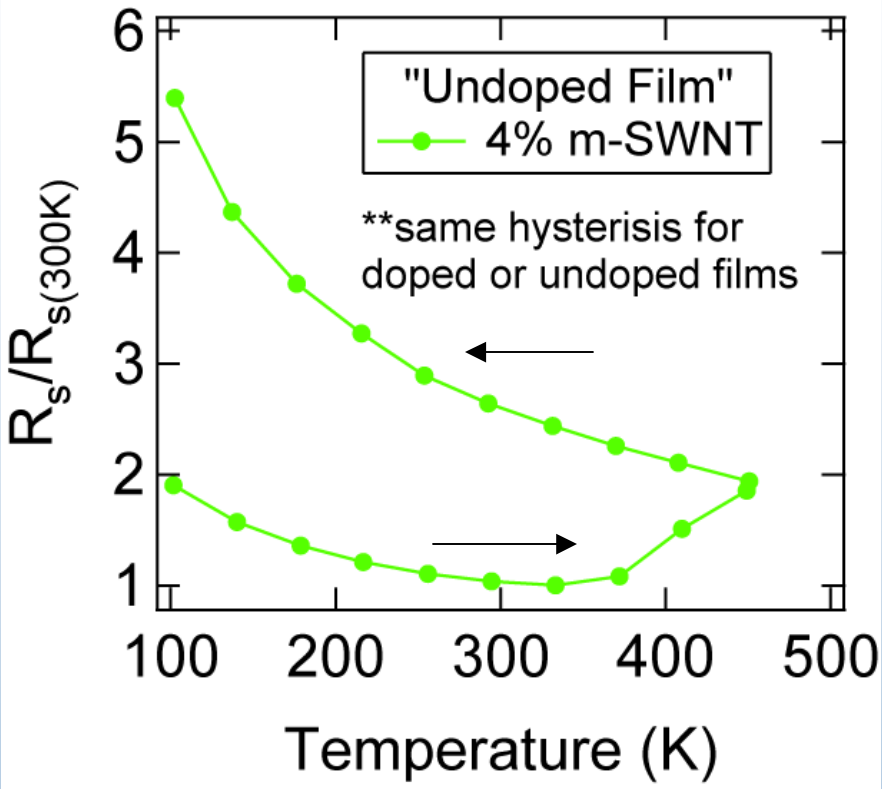
Fluctuation-assisted tunneling through barrier T_b

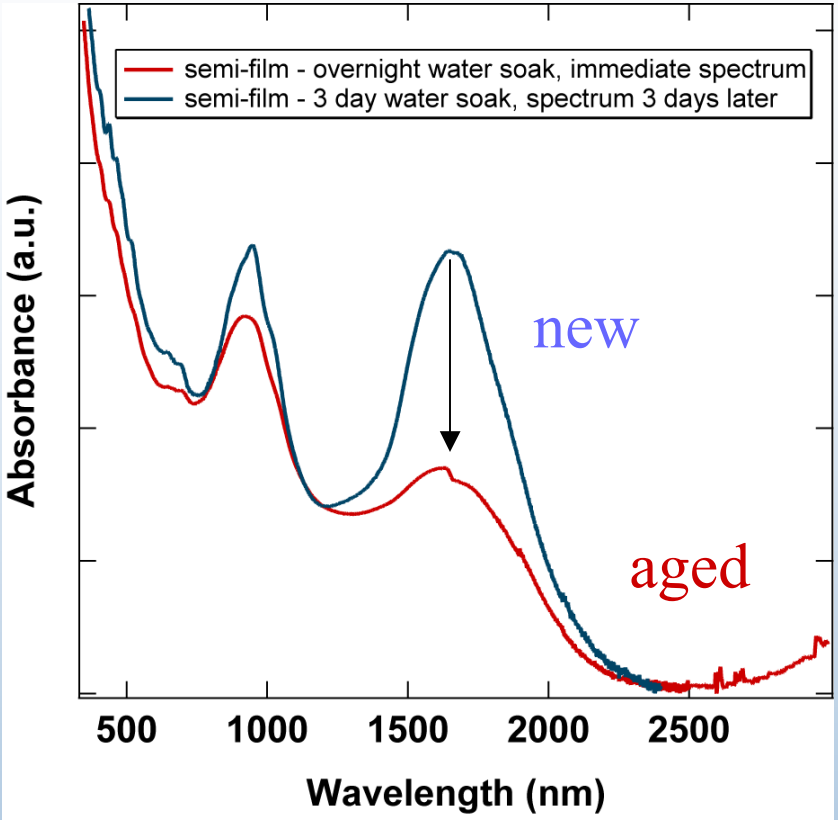
$$\beta\exp\left(\frac{T_b}{T_s + T}\right)$$

Metallic conduction limited by phonon backscattering

$$A\exp\left(-\frac{T_m}{T}\right)$$

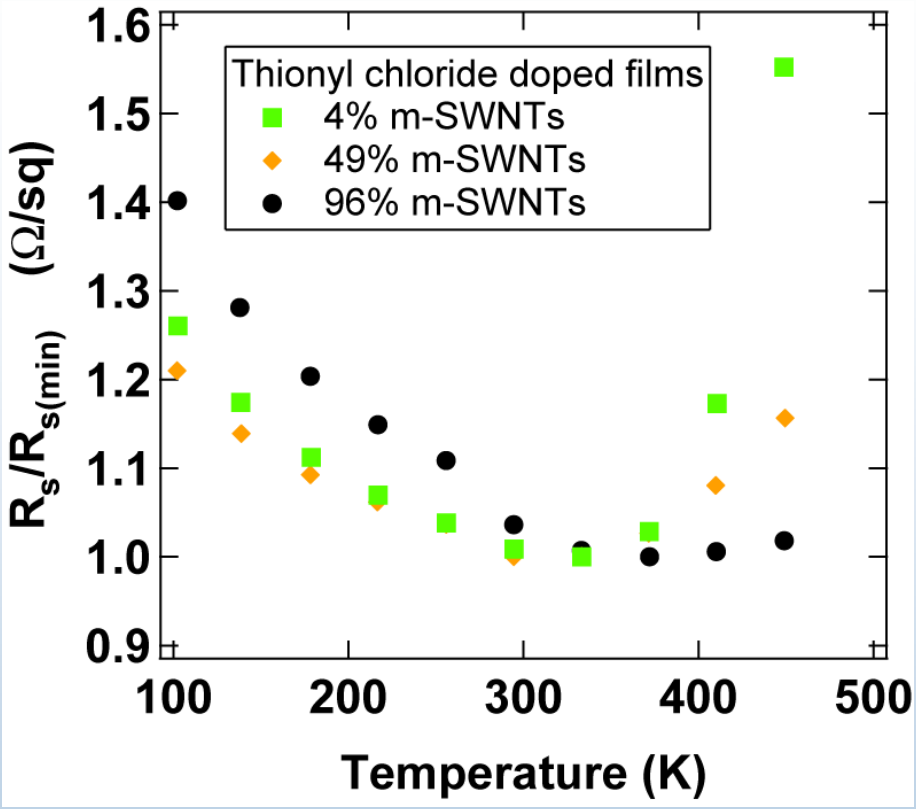
Ambient Doping Causes Hysterisis

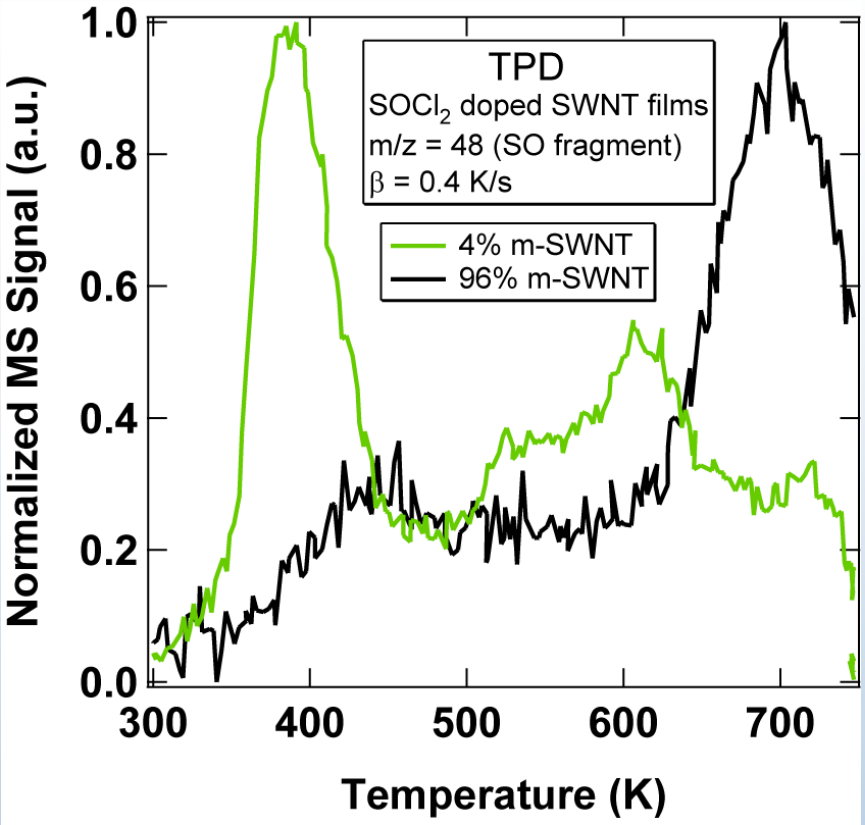




- Seen after storing in air or soaking in H_2O
- Doping by adsorption of water, protons, and oxygen
- Hysteresis in R(T) can be rationalized by dopant desorption

M-SWNTs show enhanced temperature stability



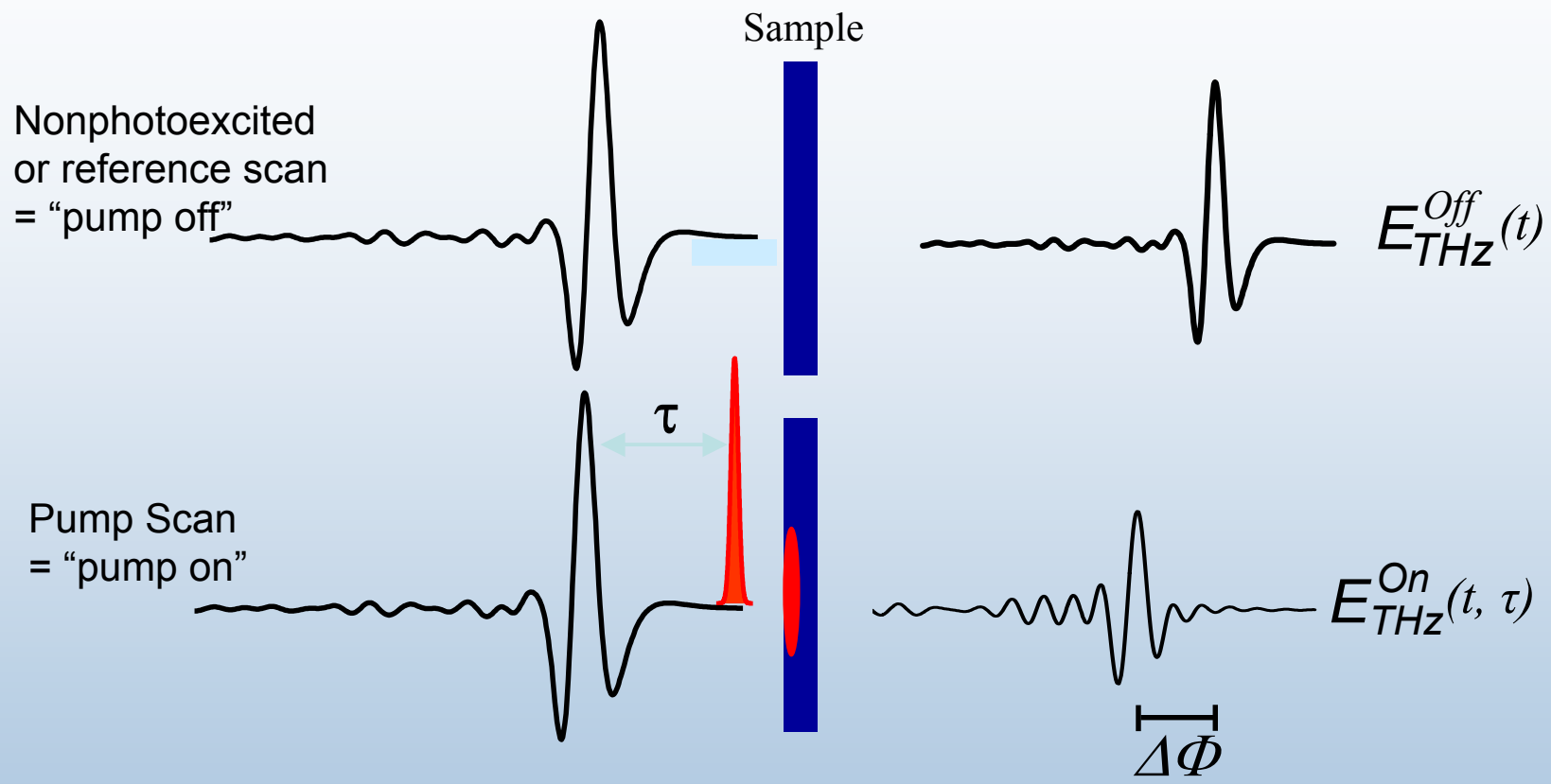


- Change of δR/δT near room T typically attributed to change to metallic behavior at high T
- M-enriched films show least "metallic" behavior
  - TPD suggests stronger binding energy for $SOCl_2$ on m-SWNTs

Conductivity

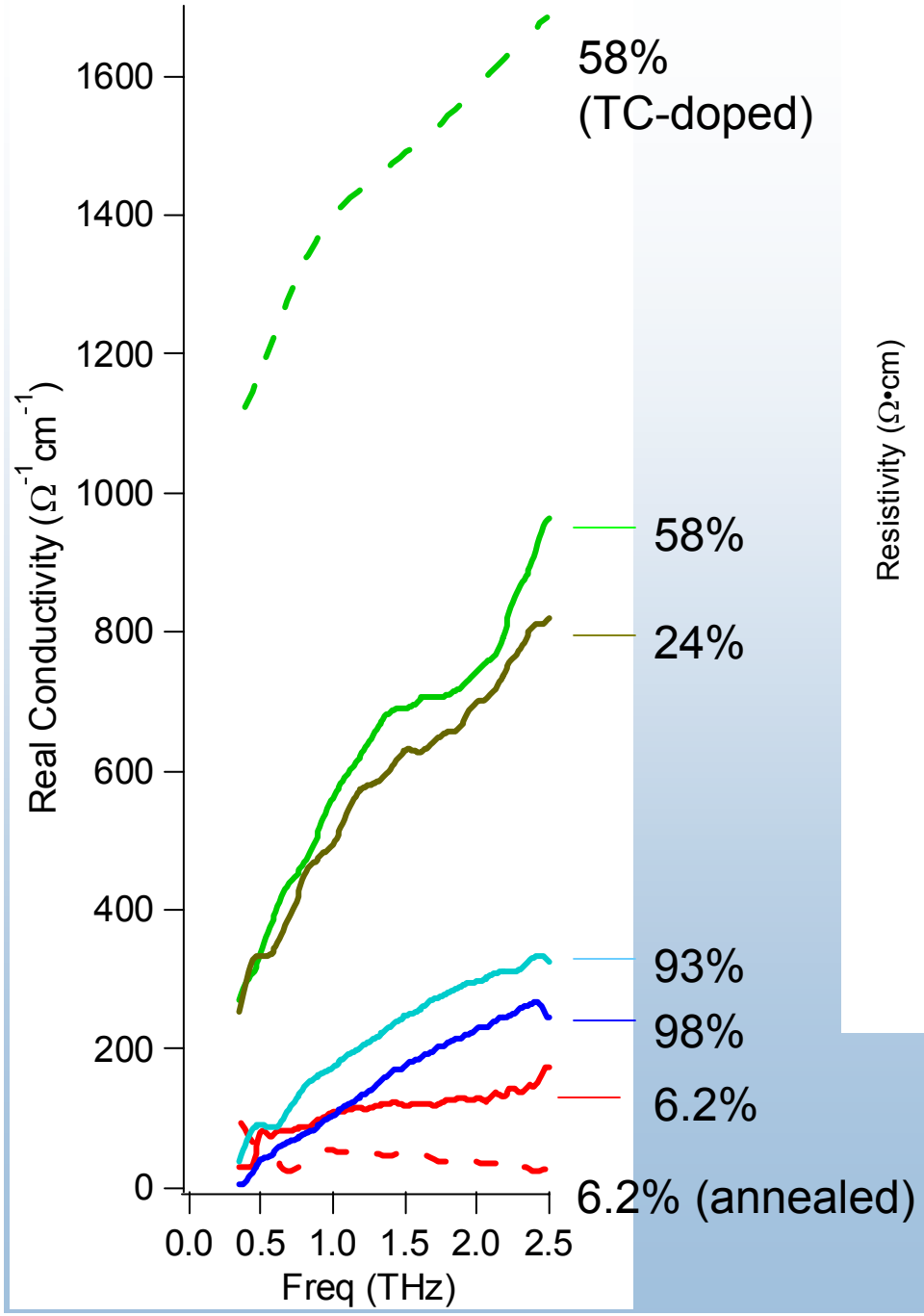
III. Terahertz Spectroscopy

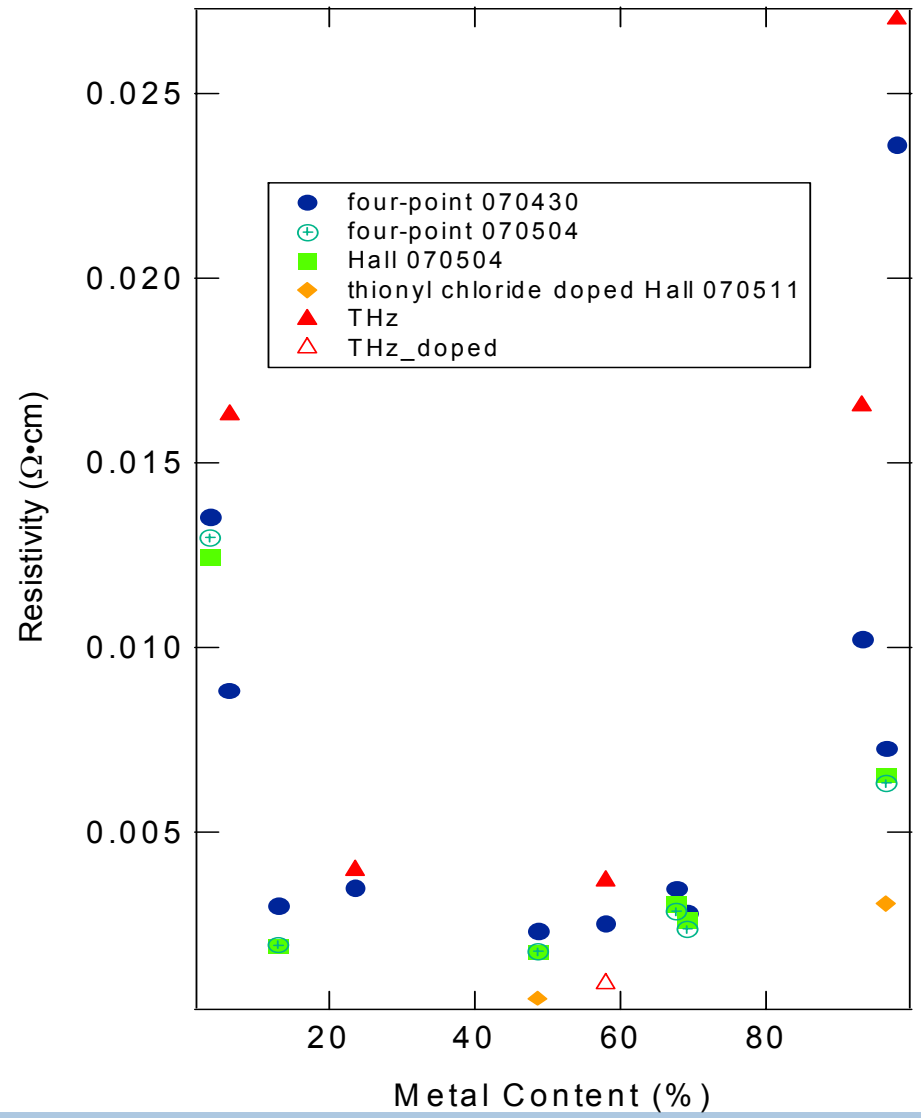
Time Resolved THz Spectroscopy



$$\frac{\Delta E_{THz}(t,\tau)}{E_{THz}^{Off}(t)} \cong \frac{-\sigma(\tau)x}{2cn\varepsilon_o}$$

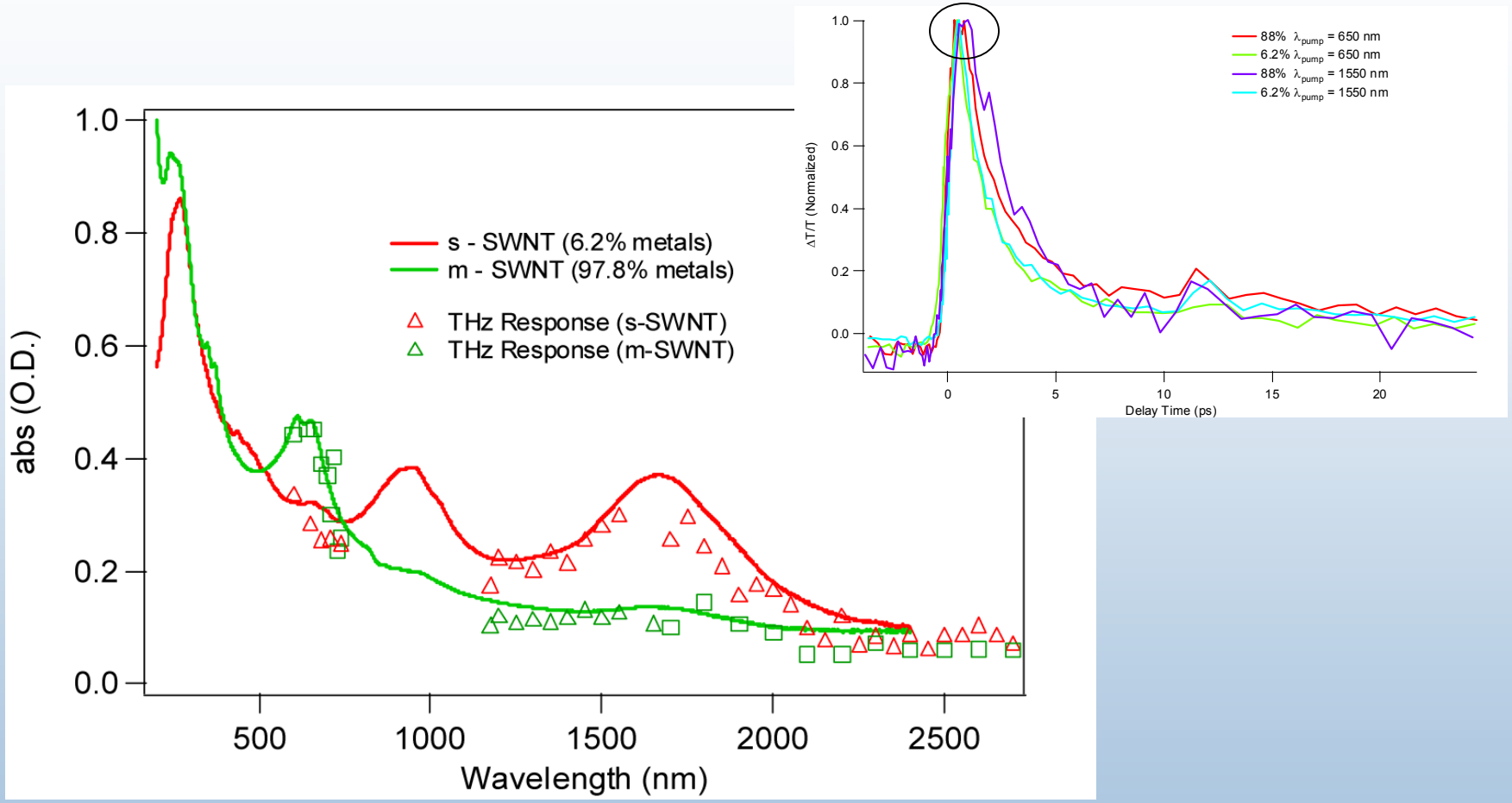
- Measure transient THz frequency average conductivity
- Subpicosecond resolution
- Mechanistic information
- No electrical contacts





- THz gives same trends as DC
- Rules out effects of contacts

Photoconductivity "Action Spectrum"



- Little dependence of photoconductivity decay time on tube type
- Amplitude of photoconductivity scales with OD of either tube type

Conclusions

- ✓ Electrical characterization of transparent conducting separated SWNT mats is complex because of many experimental parameters
  - ✓ Tube-tube contacts
  - ✓ Length
  - ✓ Intentional and unintentional doping
  - ✓ Morphology
- ✓ Can we still expect some improvements over bulk samples?
  - ✓ Doped s-SWNTs?
  - ✓ Highly pure (long) m-SWNTs?

Ongoing/Future Studies

- ❖ Time-resolved terahertz and microwave conductivity ⇒ *photoconductivity*
  - ❖ Heterojunction blends with P3HT, MEH-PPV, QDs, etc.
- ❖ Devices with Separated SWNT electrodes, and separated SWNT blends