Carbon Nanotube Vacuum Gauges Utilizing Long, Dissipative Tubes

Dr. Anupama B. Kaul & Dr. Harish M. Manohara

Jet Propulsion Laboratory
California Institute of Technology
Anu.Kaul@jpl.nasa.gov

SPIE 2008
Micro (MEMS) and Nanotechnologies for Space, Defense and Security III
Orlando, FL

Copyright 2008, California Institute of Technology
Government Sponsorship is acknowledged

Acknowledgements

Sponsors

- Defense Advanced Research Project Agency (DARPA) seedling fund (NMO#715839, NAS7-03001)

- JPL Lew Allen Award Fund for Dr. Harish Manohara

Personnel

- Mr. James Wishard for providing facilities and valuable assistance in the JPL Micro Devices Laboratory

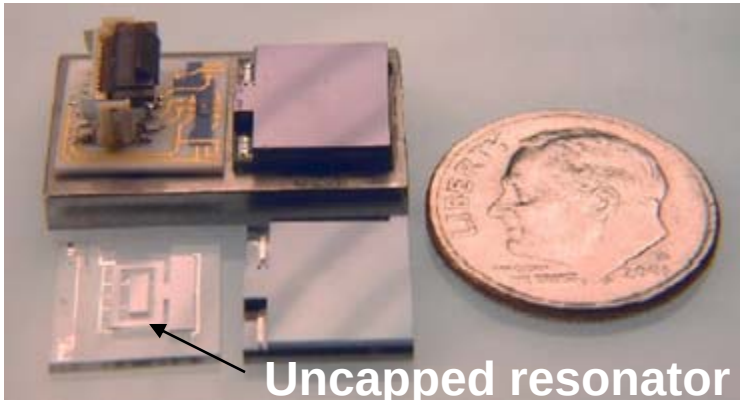
- Dr. Eric Wong for SWNT growth

- Mr. Ron Ruiz for SEM imaging

Vacuum Gauge Applications

Vacuum-Packaged Structures

- Vacuum electronics: MMW and THz vacuum electronics (e.g. amplifiers, oscillators, traveling wave tubes)
- Microgyroscopes: e.g. as resonators
- RF MEMS: e.g. switches, filters

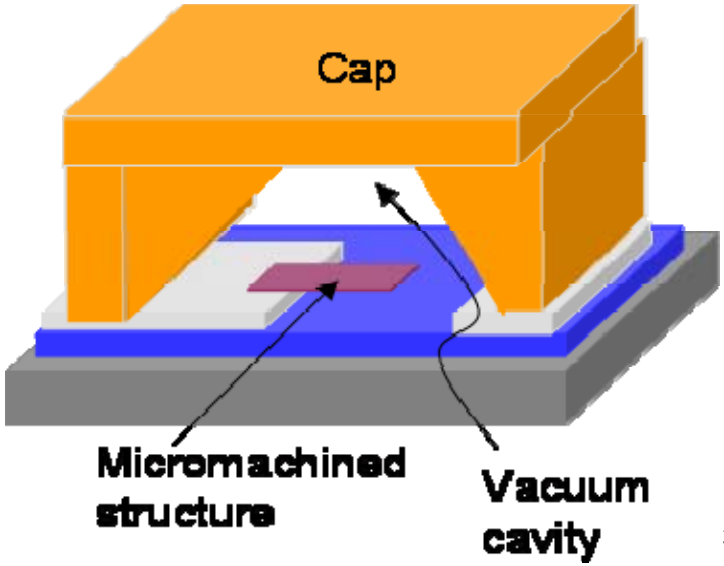


Sparks, Ansari, Najafi,
IEEE Trans. Adv. Packaging, vol. 26, 2003

Vacuum Micro-cavity

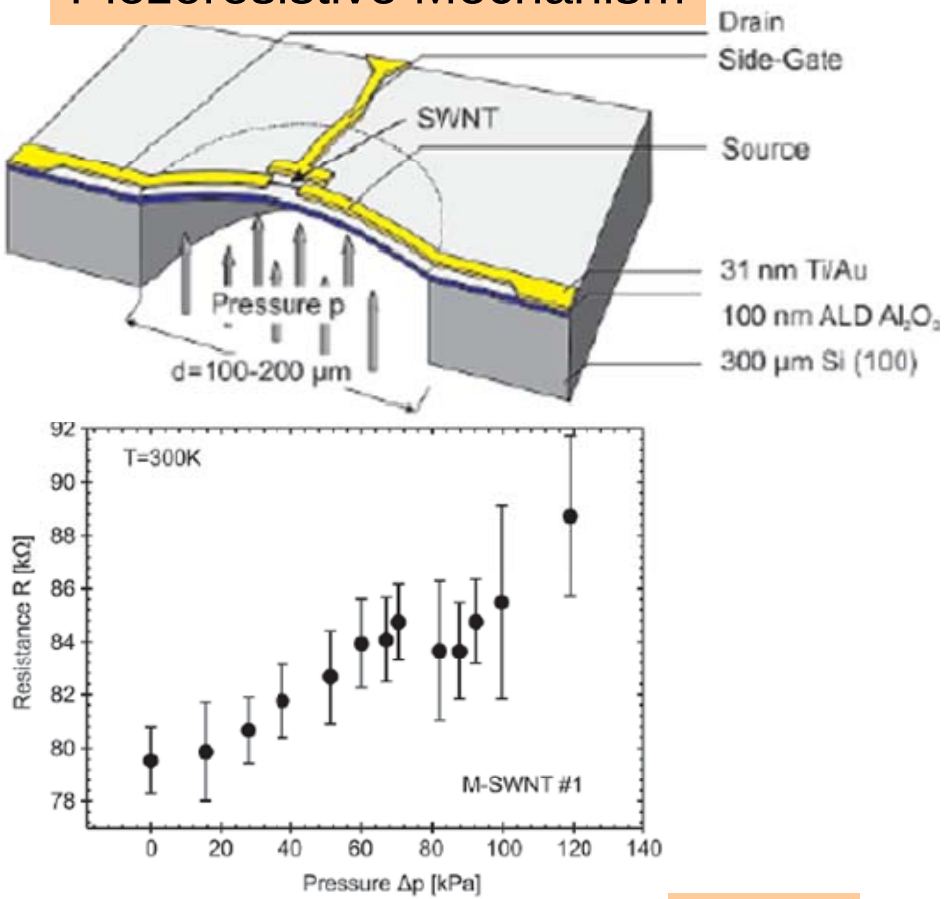
- Device performance within micro-cavity usually affected by quality of vacuum
- Small-volumes → large pressure changes from thermal excursions and gas desorption
- Miniature vacuum gauges integrated with micro-cavities can non-invasively monitor local pressures to characterize device performance over product lifetime

Vacuum Micro-cavity



Carbon Nanotube Pressure Sensors

Piezoresistive Mechanism



C. Stampfer, C. Hierold, *et al. Nano Lett.*, vol. 6, 2006.

Electrothermal CNT Gas Sensor Reported: T. Kawano, L. Lin, *et al. Nano Lett.*, vol. 7, 2007.

Piezoresistive Mechanism

- Metallic SWNTs on ALD-deposited membranes of Al_2O_3
- Pressure differential causes membrane to bulge, inducing strain in overlying SWNT

This Work: Thermal Conductivity Mechanism

- Heat transferred to gas function of pressure for sensor held at fixed bias

$$E_{Total} = E_{substrate} + E_{radiation} + \boxed{E_{gas}}$$

- Small dimension of CNT and large TCR values enables greater pressure sensitivity
- Non-intrusive: low power, small-size, promising for micro-cavities

Device Fabrication Facilities

JPL's Microdevices Laboratory: 12,000 square feet class 10 cleanroom

Contact lithography units

JEOL E-beam aligner
Canon Excimer Laser DUV Stepper

Conventional
RIE etchers (CF_4/BCl_3)

ICP etchers: high density, low pressure plasma (chlorine and fluorine chemistries)

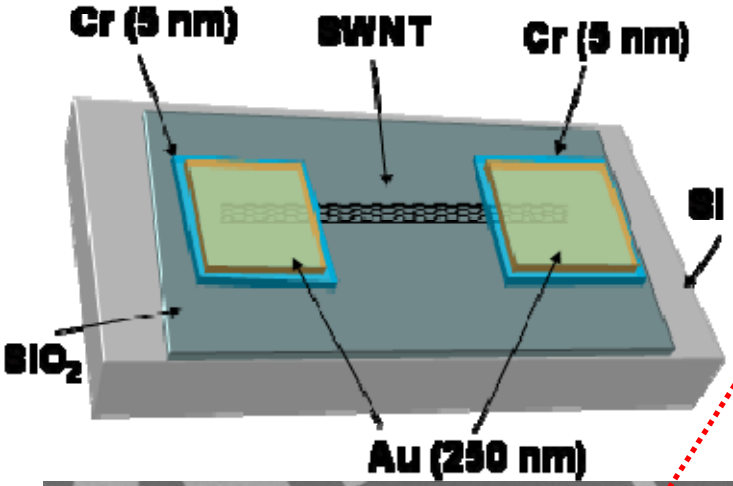
Dektak profilometer

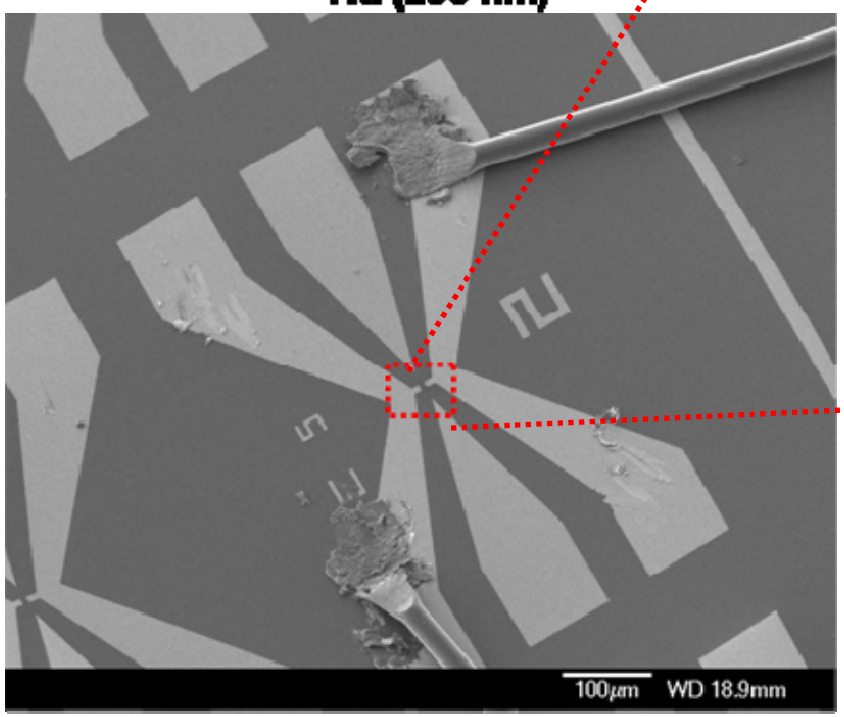
E-beam evaporator (Pt, Ti, Au electrodes)

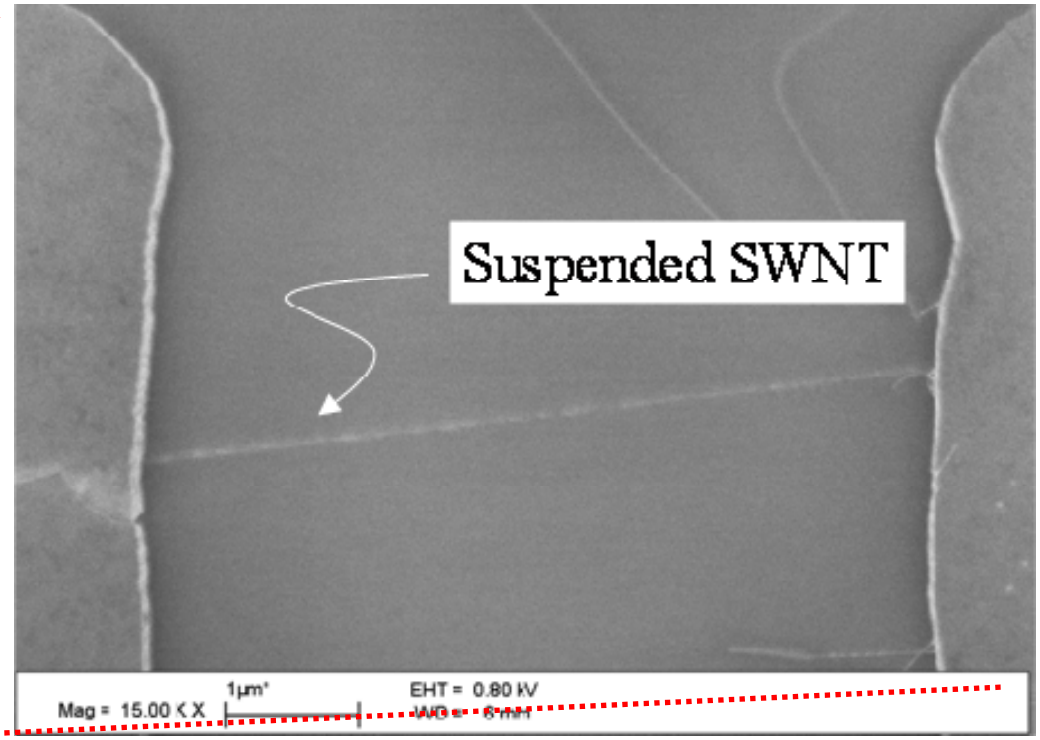
Other key equipment:

-dc magnetron sputtering system
-CVD furnace (CNT growth)
-Fe e-beam evaporator (catalyst layer)
-PECVD dielectric deposition
-AFM, SEM (CNT imaging, characterization)

Fabricated Devices



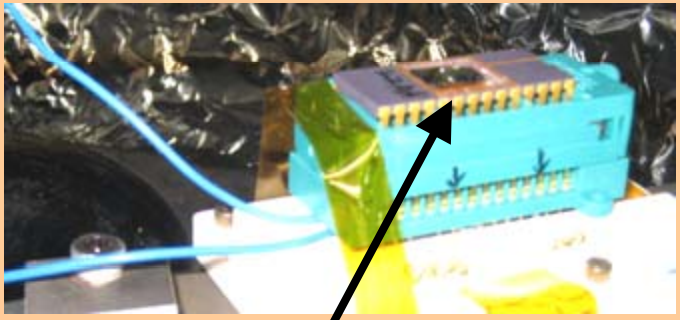




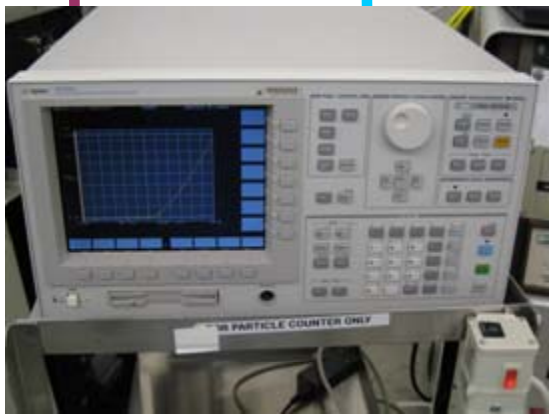
Measurement Set-up

Computer interface to parameter analyzer using ICS data acquisition software; current sampled at 1 sec intervals at fixed bias voltage

Bell-jar



Devices wire-bonded on chip-carrier



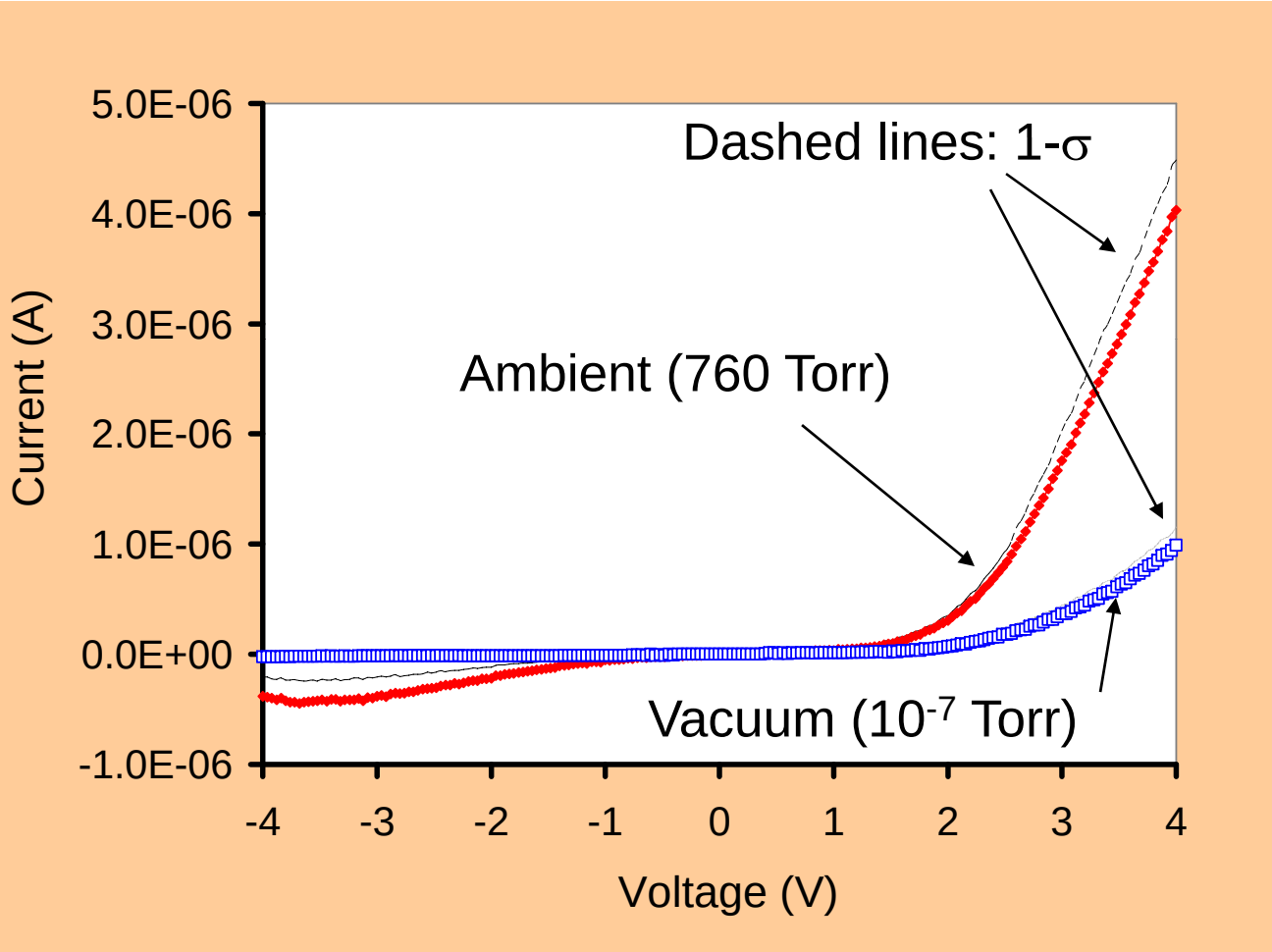
HP 4156C Parameter Analyzer

coaxial cables

Electrical feed through for 2-terminal measurements

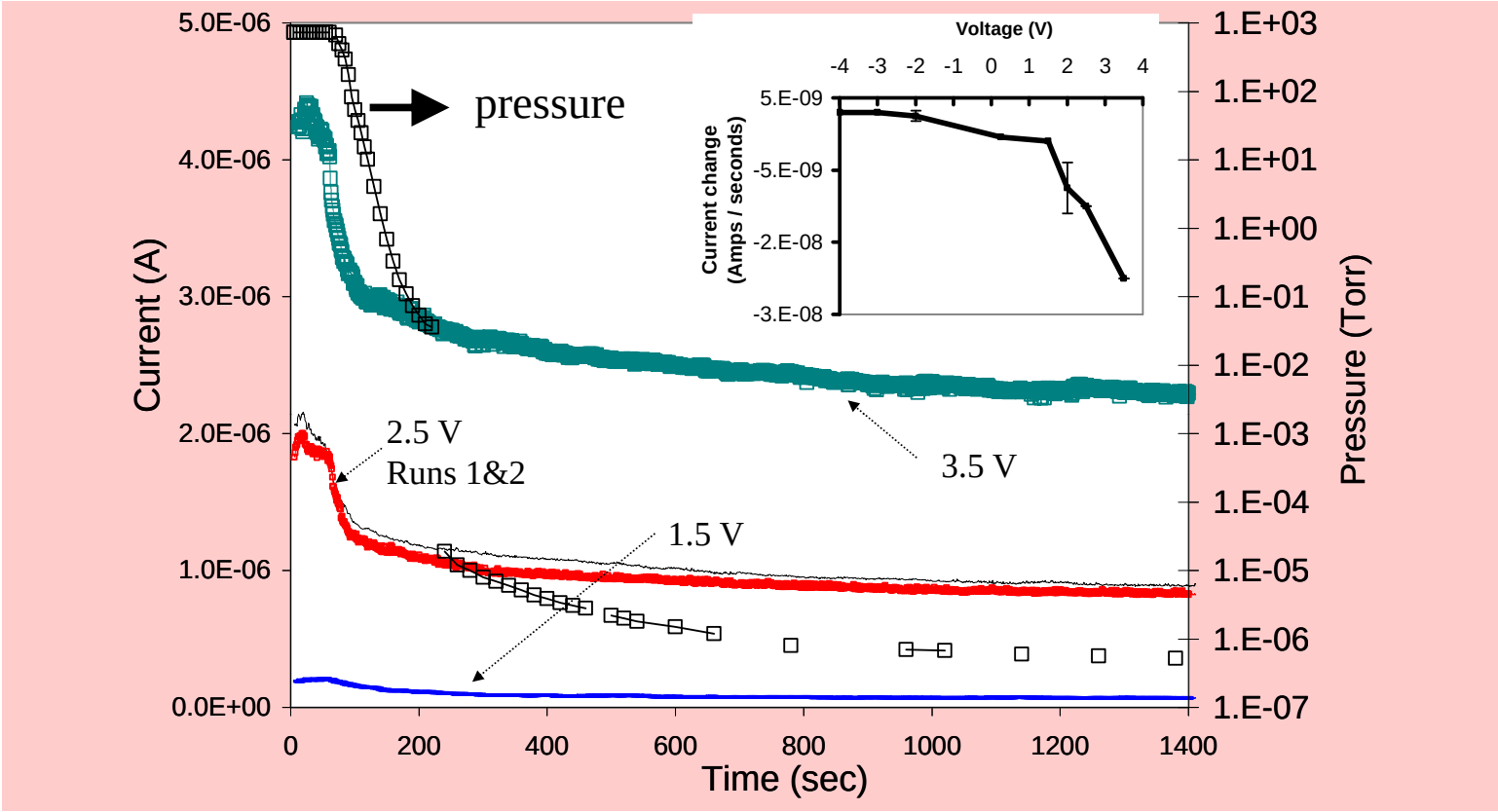
- Wheatstone bridge not required, sensitivity ~10 pA on analyzer
- Mechanical pump (760 Torr – 35 mTorr); pressure measured with convectron gauge
- Ultimate pressure ~ 10^{-7} Torr (cryo pump); pressure measured using ion gauge

Static Pressure Response



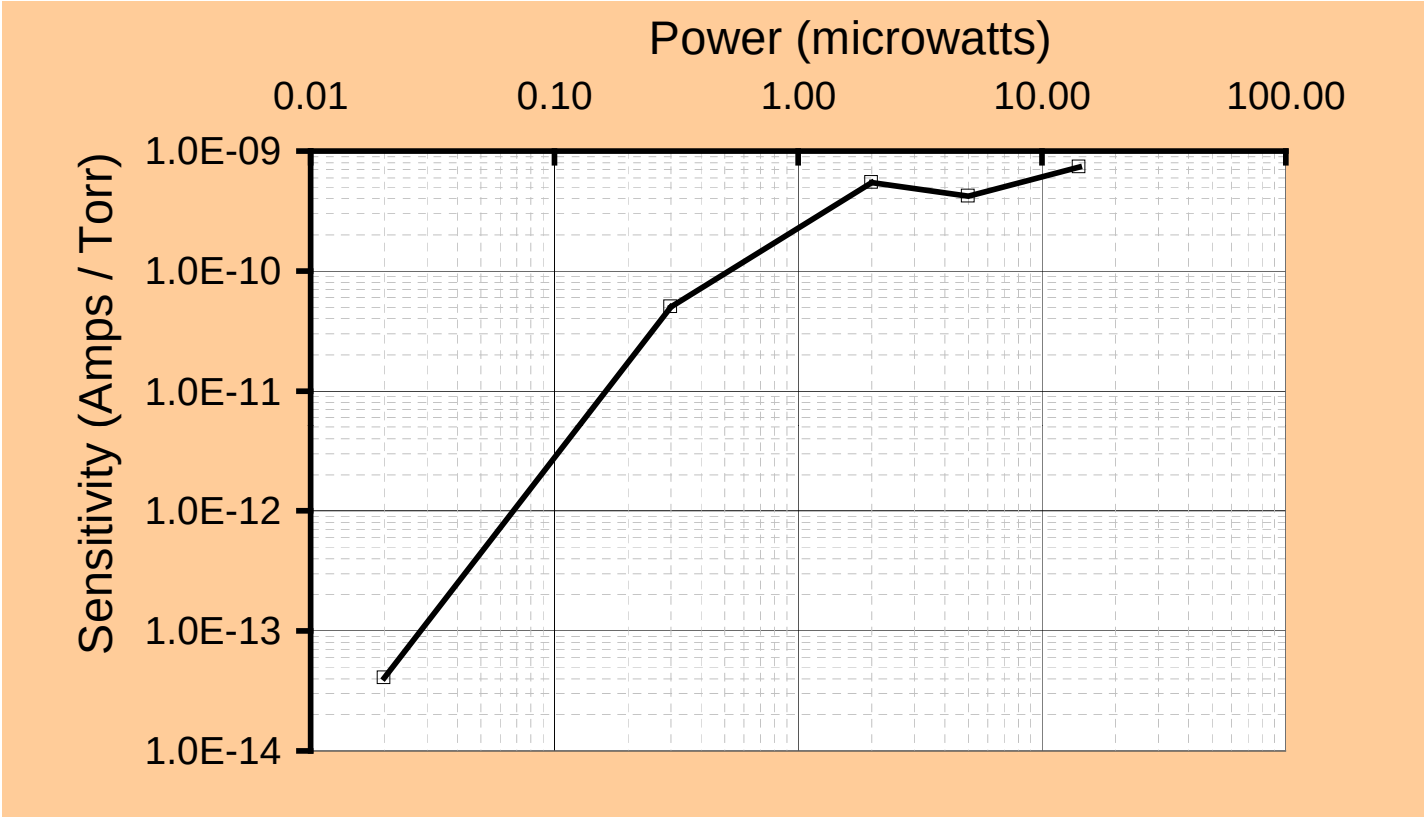
- Reduced conductance at low pressures
- Change in I detected from 760 Torr – 10^{-7} Torr
- Good repeatability
- Stable over weeks, contacts do not change irreversibly despite high resistances
- Earlier Ti-contacted CNTs less stable with pressure cycling (possibly due to propensity of Ti for oxidation)

Dynamic Pressure Response



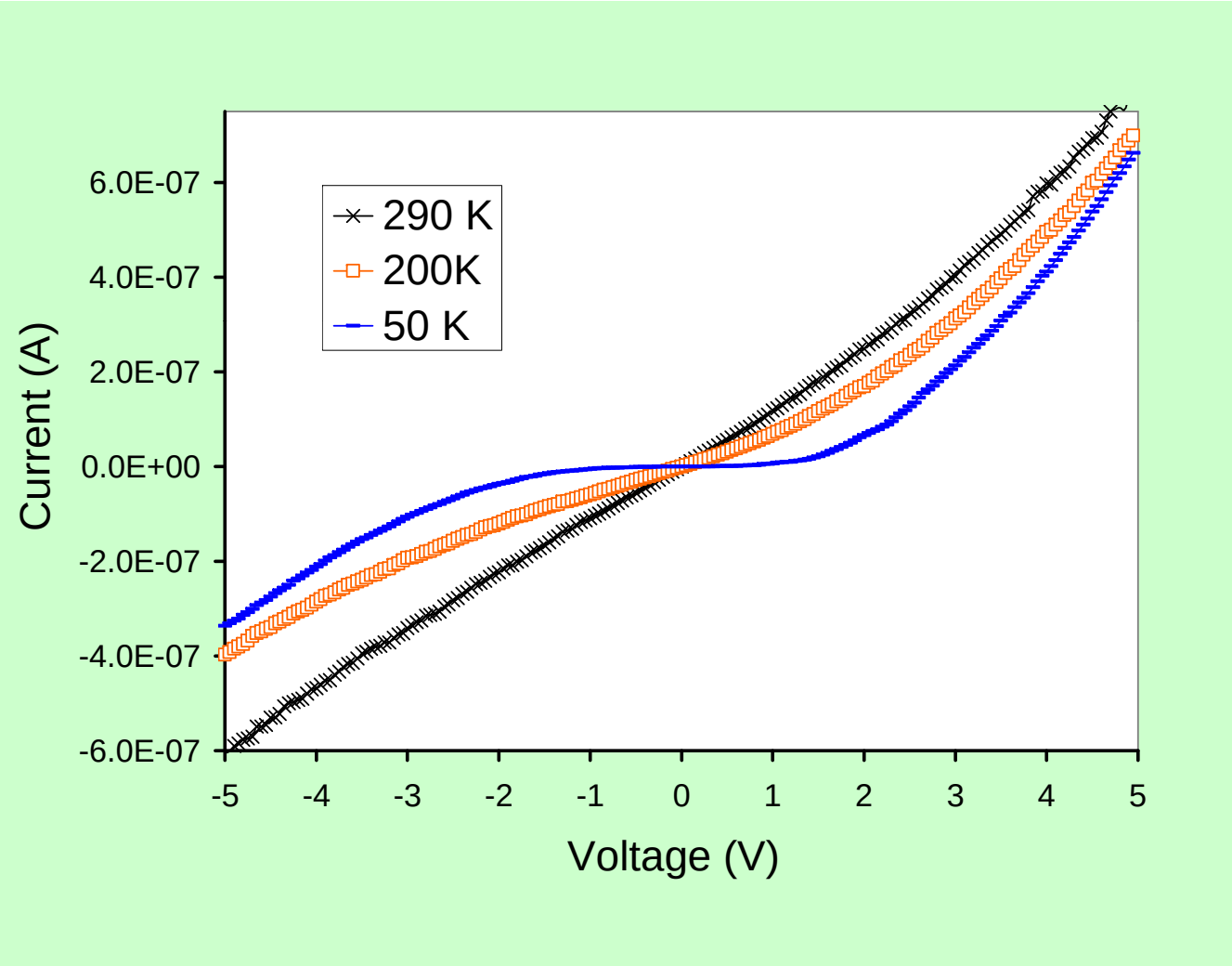
- Conductance decreases rapidly initially (760 Torr - 1 Torr) for all biases
- Response less sensitive at lower pressures; molecular collision rates higher at higher pressures → greater cooling, greater current change
- As bias voltage increased, rate of current change increases in linear regime (inset)

Pressure Sensitivity with Power



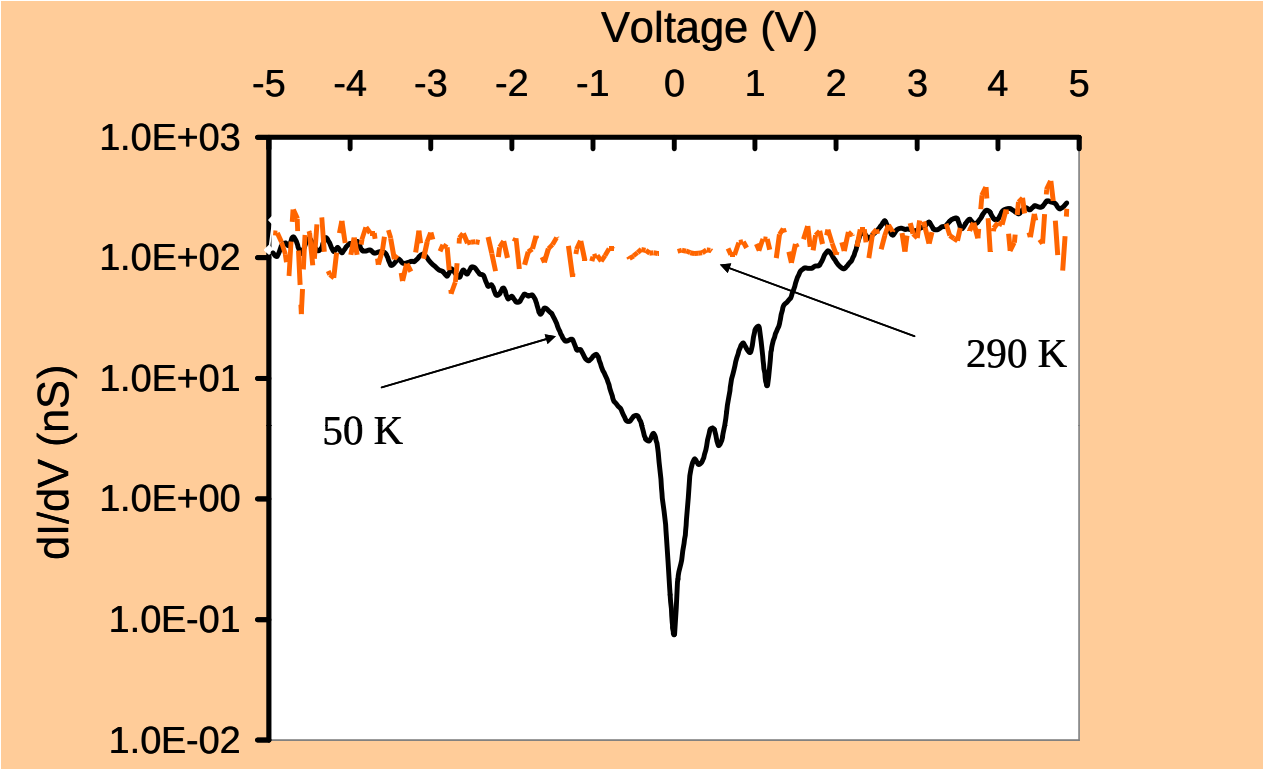
- Sensitivity increases with power (temperature changes higher)
- At powers as low as 20 nW, measurable sensitivity ~ 40 fA/Torr
- Increases up to ~ 1 nA/Torr at ~ 14 μW
- Earlier thermal conductivity gauges show similar behavior but at > mW-levels of power

Low temperature transport



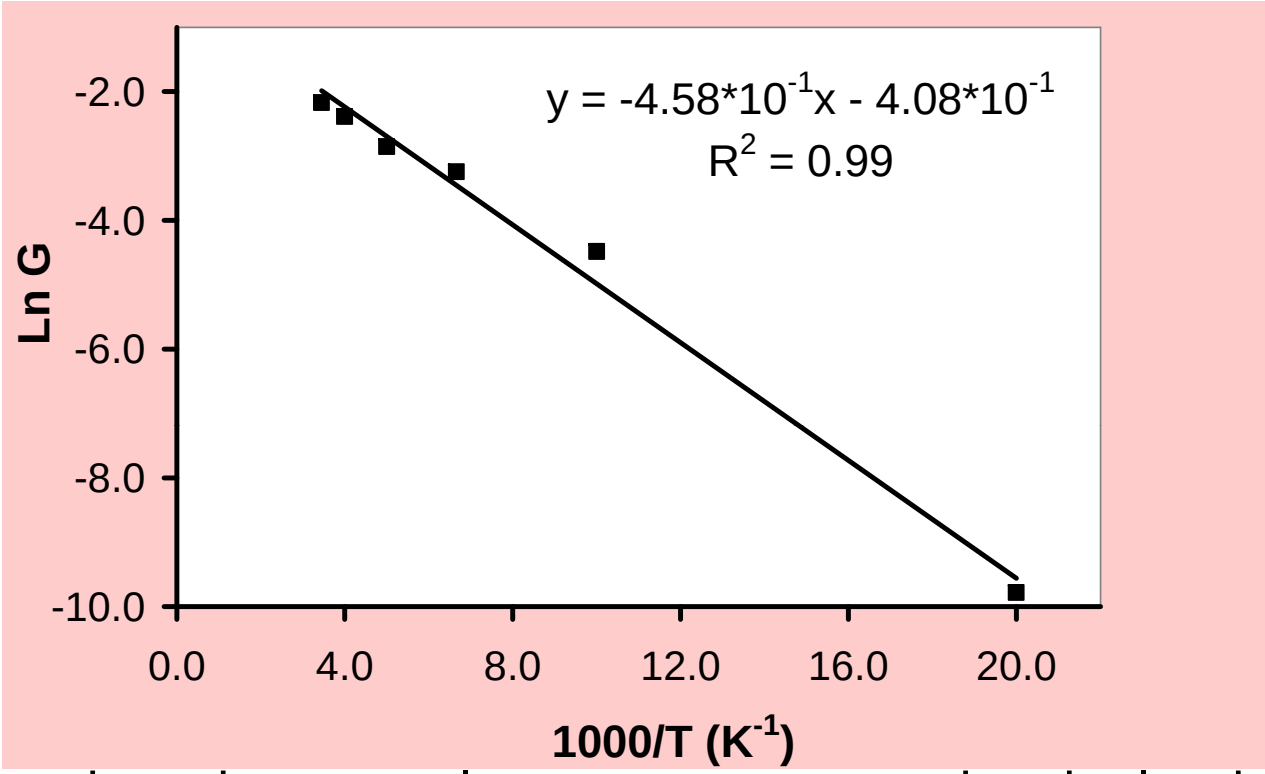
- I-V characteristic predominately linear at 290 K.
- Slight non-linearity at 200 K begins to emerge at low bias voltages
- Non-linearity gets more pronounced at ~ 50 K

Low bias conductance



- At 290 K, conductance independent of bias voltage (as expected).
- At 50 K conductance suppression observed at low bias
- Gap formation occurs for V below ~ 1.5 V at 50 K, where conductance is suppressed by more than 3-orders of magnitude, converges to 290 K value
- $G = T.\frac{4e^2}{h}$ T << 1 low transparency contacts, CNT weakly coupled to leads
- Luttinger liquid behavior $G \prec T^{\alpha}$ (α = 0.33-0.38) did not fit data well

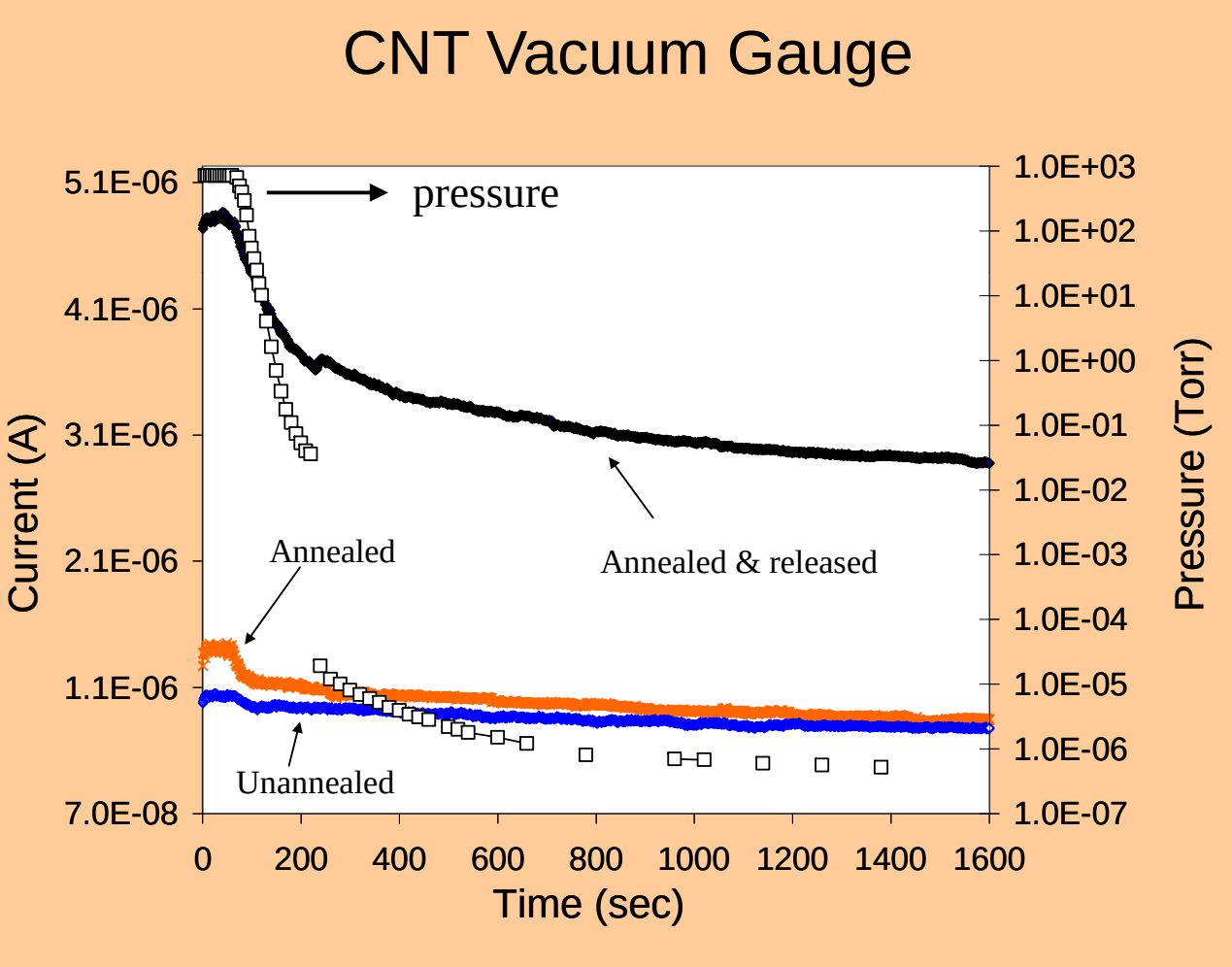
Thermally Activated Hopping Mechanism



- Suppressed conductace at low temperatures and under low bias conditions could arise from several mechanisms
- Potential barrier at contacts suggesting CNT weakly coupled to the leads (coloumb blockade)
- Defects in long tubes (bends, etc.) leads to suppressed conductance
- Electron localization due to defects (thermally activated transport) $LnG \prec \frac{-E_a}{k_B T}$ provided a good fit to data where hopping energy, E_a ~ 39.5 meV

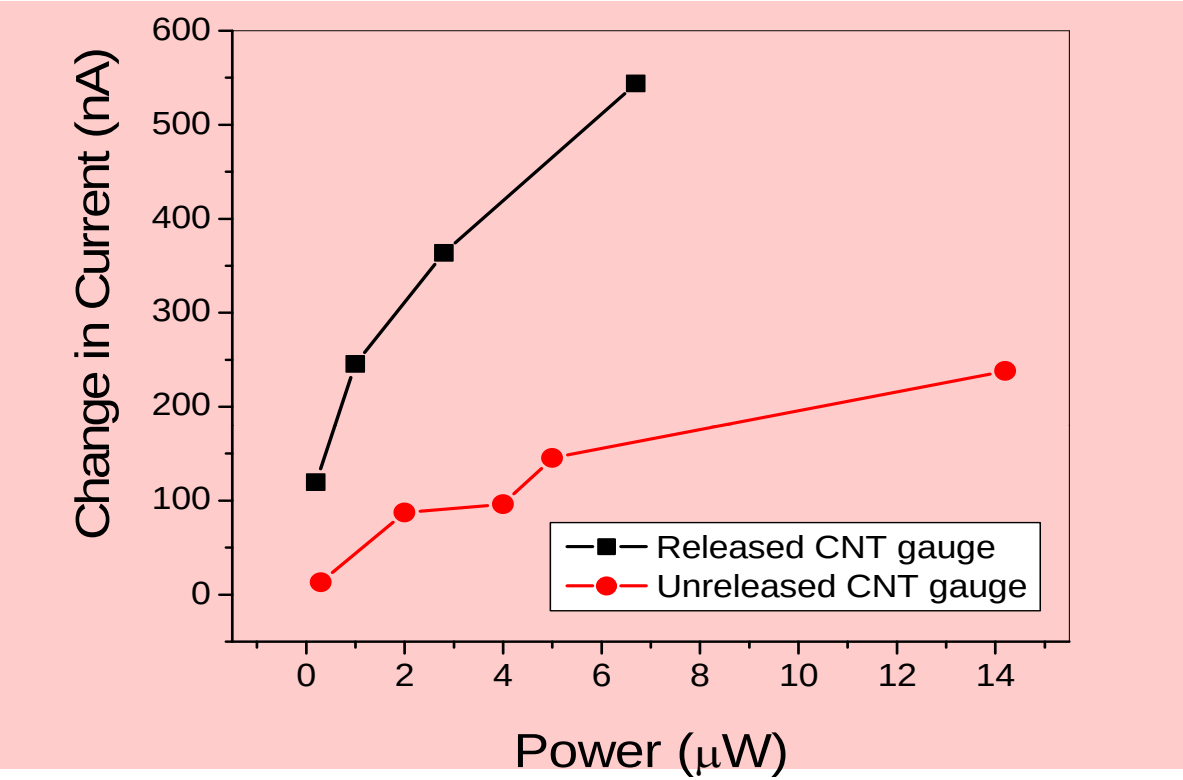
Substrate removal

$$E_{Total} = E_{substrate} + E_{radiation} + E_{gas}$$



- Losses through substrate important at low pressures
- CNT devices released in 10:1 BOE and critical point drying to remove thermal SiO_2 underneath
- Annealed and released device continued decrease in current down to 10^{-5} Torr

Effect of Power at High Vacuum



- Effect of power on unreleased and released CNT devices
- Net current change ΔI measured for pressure change from 5×10^{-6} Torr to 8×10^{-7} Torr
- Released CNT device has the highest ΔI ~ 550 nA compared to ~ 150 nA for unreleased CNT device at ~ 6 μW

Summary and Future Work

CNT Vacuum Gauges

- have a broad range of pressure response from 760 - 10^{-6} Torr
- have current changes ~ 100's nA in high vacuum regime (10^{-6} Torr) and sensitivity increases with power and substrate removal
- have a negative dR/dT (TCR negative) where a thermal hopping energy E_a was determined to be ~ 40 meV.
- have compatible fabrication requirements for their integration with micromachined structures
- can be operated at low power (nW – μW)
- have an active device region footprint of < 10 μm^2
- are non-intrusive due to small size and passive operation

Future Work

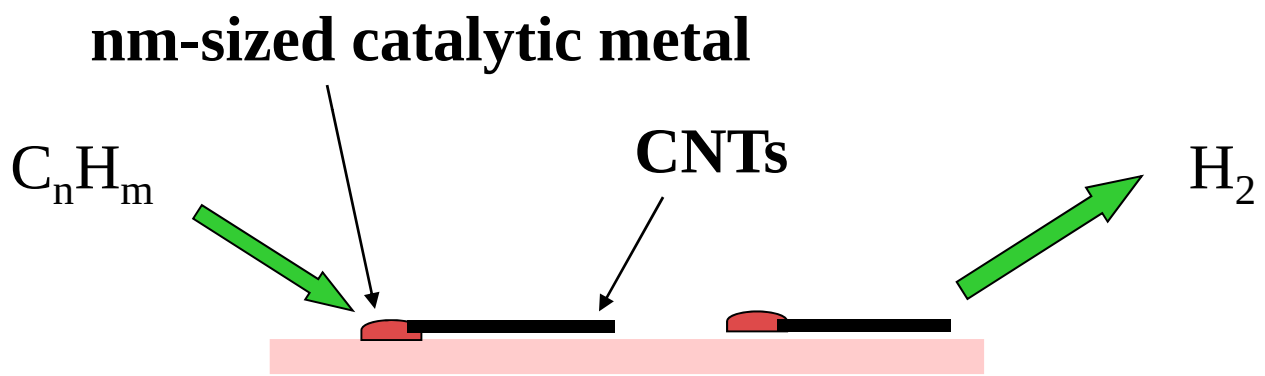
- Further work is necessary to fully characterize the effects tube characteristics (chirality, length, transparency at the contacts) have on pressure response of devices

Backups

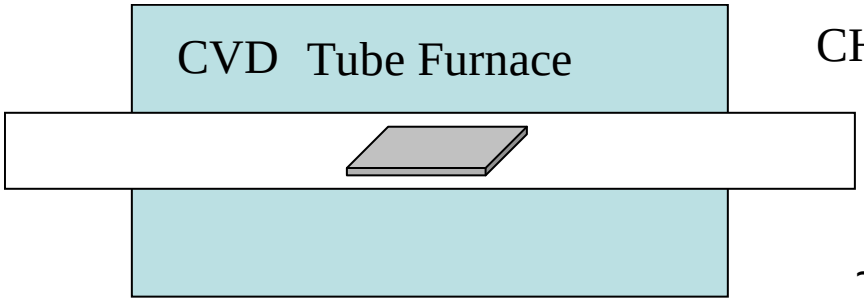
Catalytic CVD Growth of CNTs

High solubility of C in catalyst at high temperatures

Hydrocarbons (C_nH_m) $\xrightarrow[\text{600-800 C}]{\text{Fe (or Ni, Co, etc.)}}$ **C(s) + H_2**



SWNT Synthesis Conditions

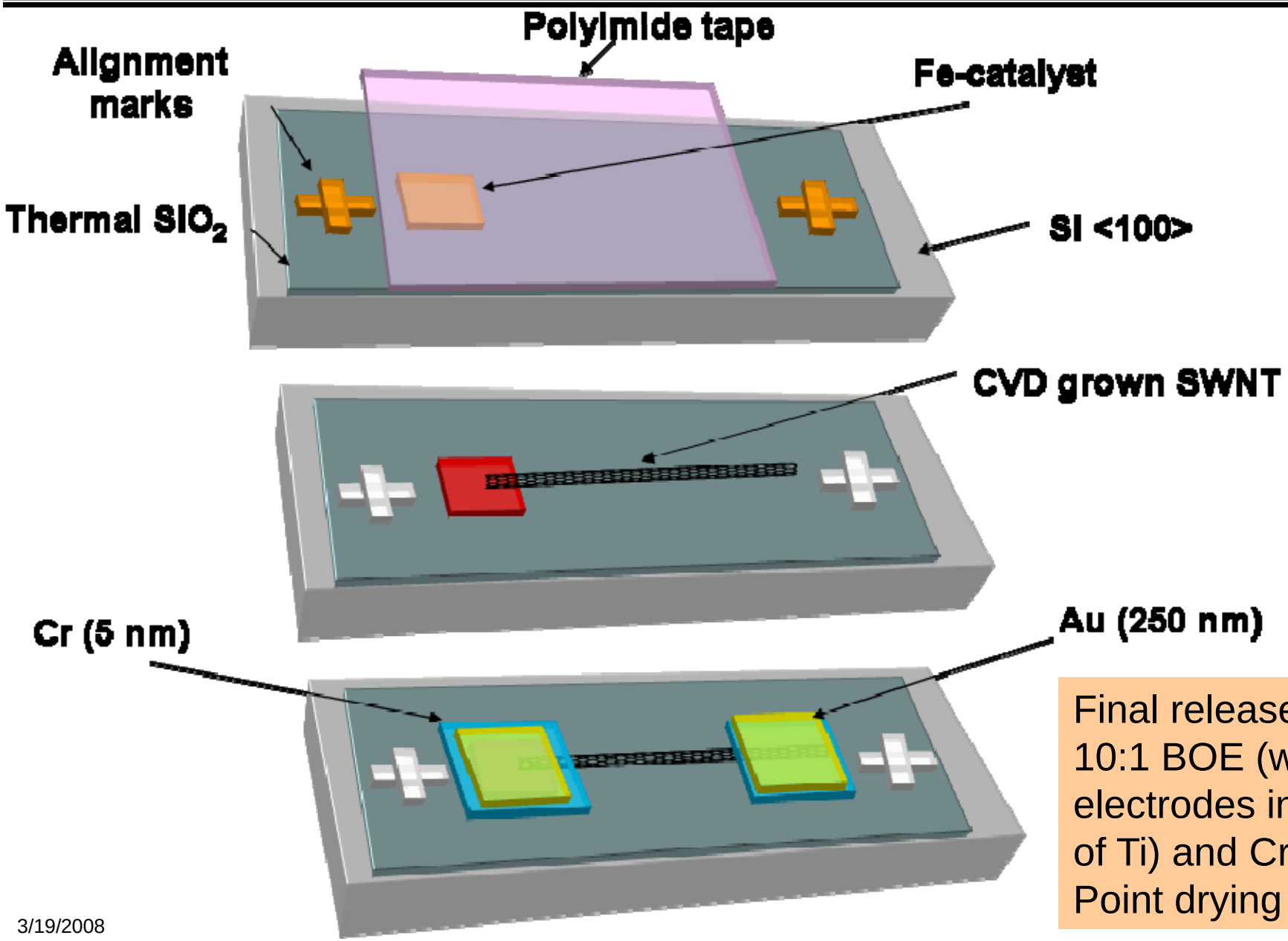


CH_4 1500 sccm & H_2 50 sccm @ 850 ºC

2” Quartz Tube

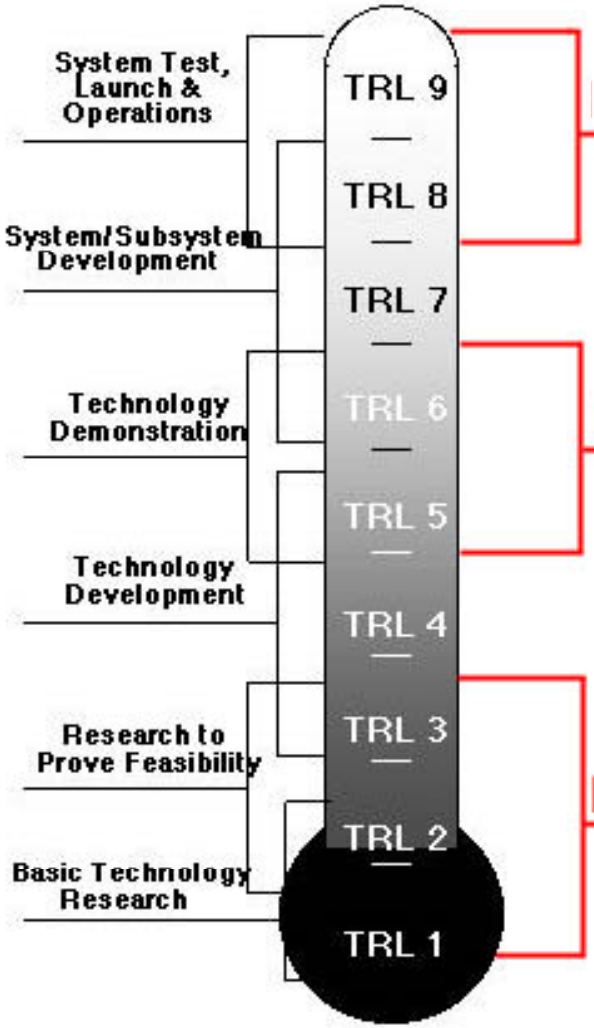
~ 1 nm thick Fe-catalyst film

Formation Process



Final release in 10:1 BOE (with Cr electrodes instead of Ti) and Critical Point drying

NASA Technology Development



Flight technologies

Mid-level technologies

Early level technologies

This work:
Feasibility study of CNT-based vacuum gauges

Conventional Pressure Sensors

Pirani, Ion Gauges

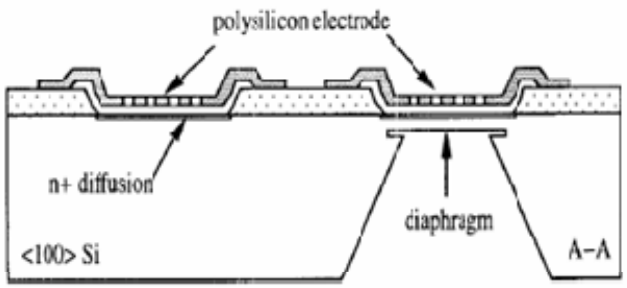
- Sensitivity good at UHV conditions
- Large volume, high power: invasive
- Difficult to integrate with micro-cavities

MEMS-based pressure sensors

- Low power, small volumes
- Mechanisms: capacitive, piezoresistive, optical determination of membrane deflection, resonance frequency shift, radio-isotope based pressure sensors
- Wide-dynamic range challenging

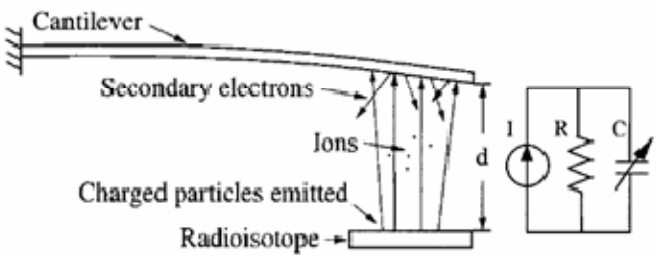
Proposing: Carbon nanotube based thermal conductivity vacuum gauge

Diaphragm-based for capacitive, Piezoresistive, optical sensing



Mastrangelo, Zhang, Tang, *J. MEMS*, vol. 5, 1996

Recently: Radio-isotope charged cantilever for sensing



A. Lal *et al. J. Appl. Phys.* vol. 92, 2002.
H. Li and A. Lal, *Proc. of the 12th Int. Conf. on Solid State Sensors, Actuators and Microsystems*, vol. 1, 2003.

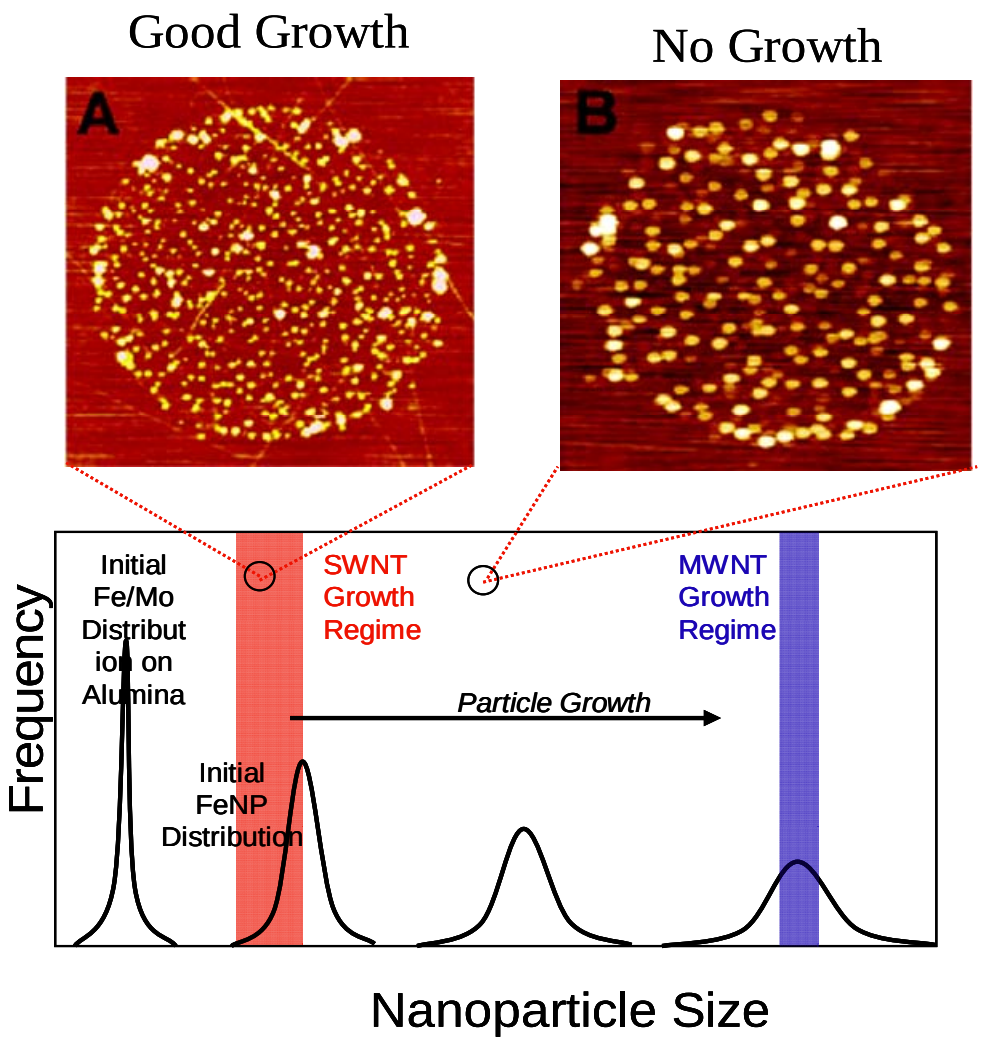
CVD Synthesis of SWNTs

Role of H_2

- H_2 required to minimize amorphous carbon, but too much H_2 or hot annealing causes particle fusion and inhibition of SWNT growth
- Particle growth desirable for larger MWNTs

Gas flow dynamics

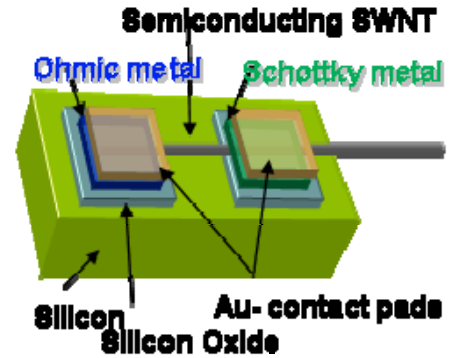
- Stagnant zone in boats results in variable gas mixing leading to variable SWNT yield
- Flat top holders with laminar flow give consistent results



Wong, E.W. *et al.*, *Chem. Mater.*, **17** (2005) 237-241

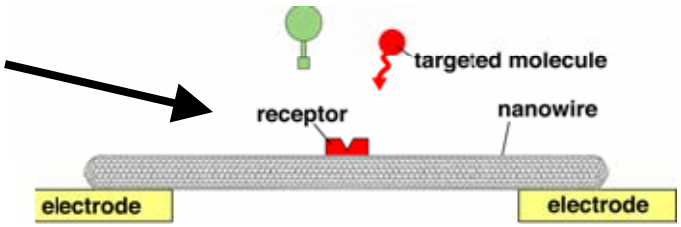
JPL CNT Device Efforts

- CNT schottky diodes for THz detectors (H. Manohara, E. Wong et al.)

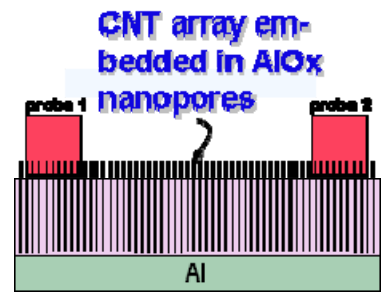


- CNT field emitters for THz sources (H. Manohara, M. Bronikowski)

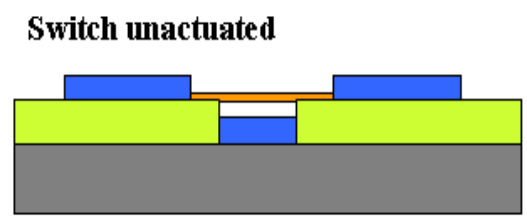
- Nanowire-based chemical spectrometer for molecular ID (B. Hunt, E. Wong, M. Bronikowski, et al.)



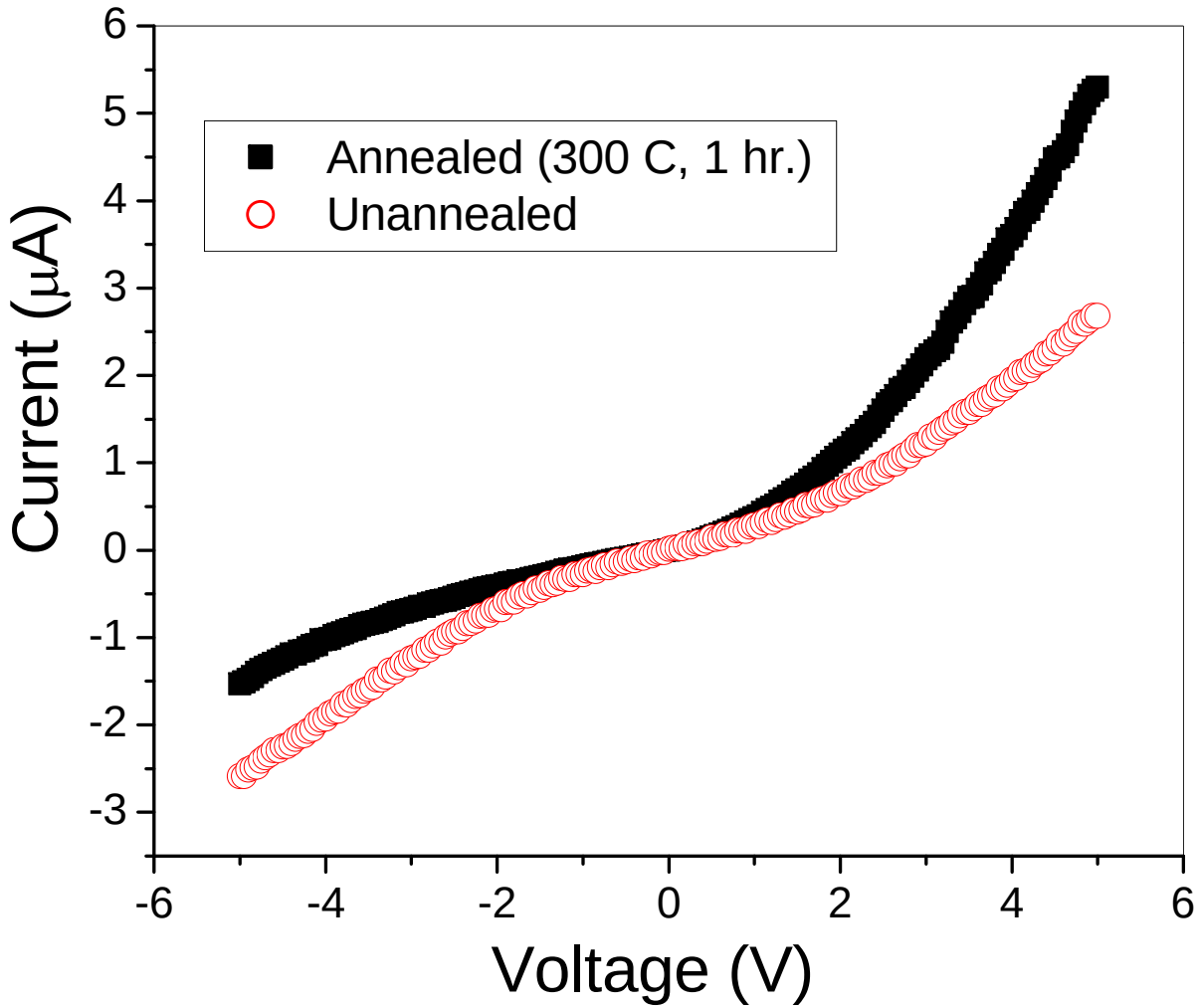
- CNT mechanical resonators for RF signal processing (B. Hunt, L. Epp et al.)



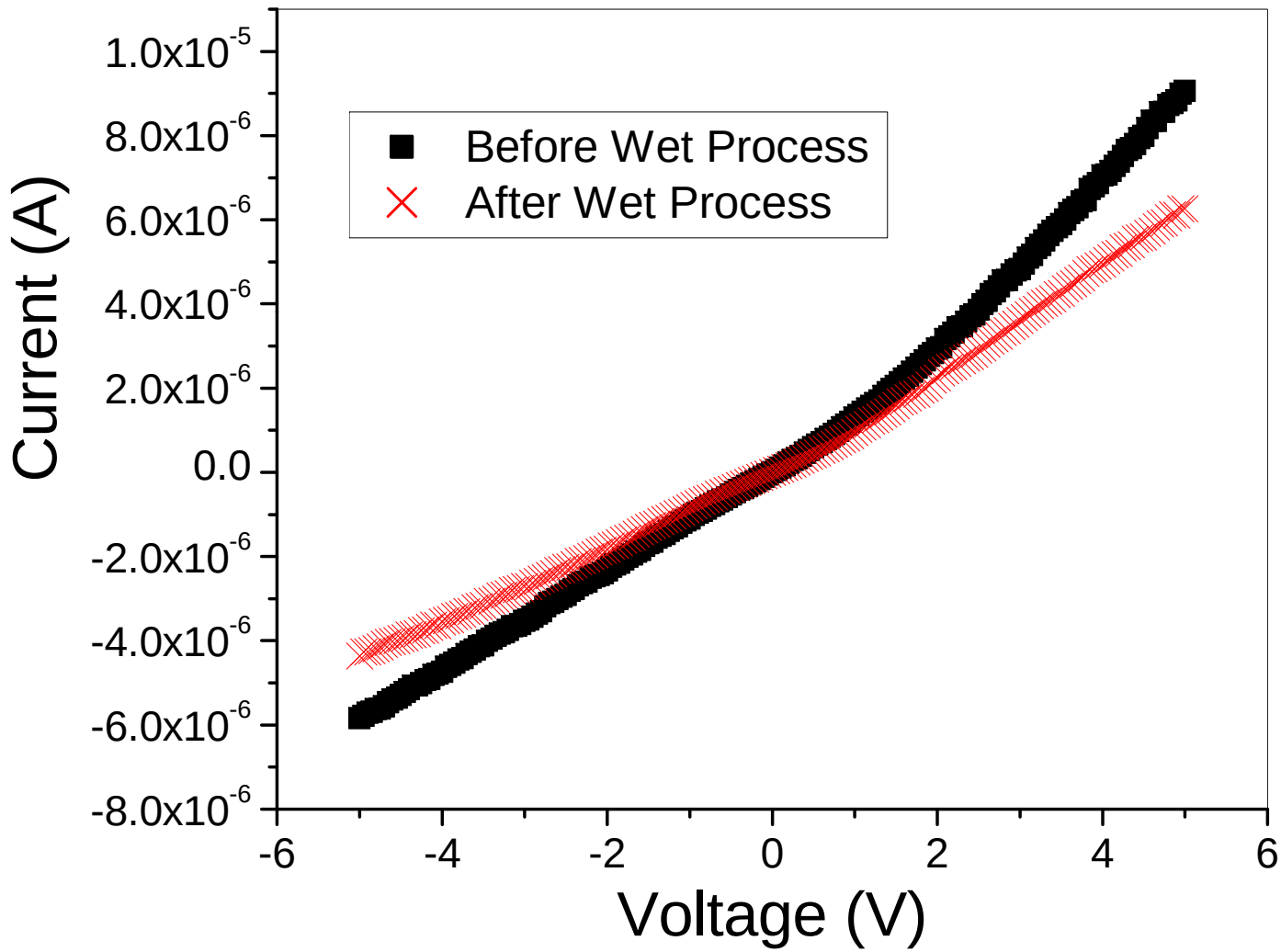
- CNT switches (A. Kaul, E. Wong, et al.)



Effect of Annealing

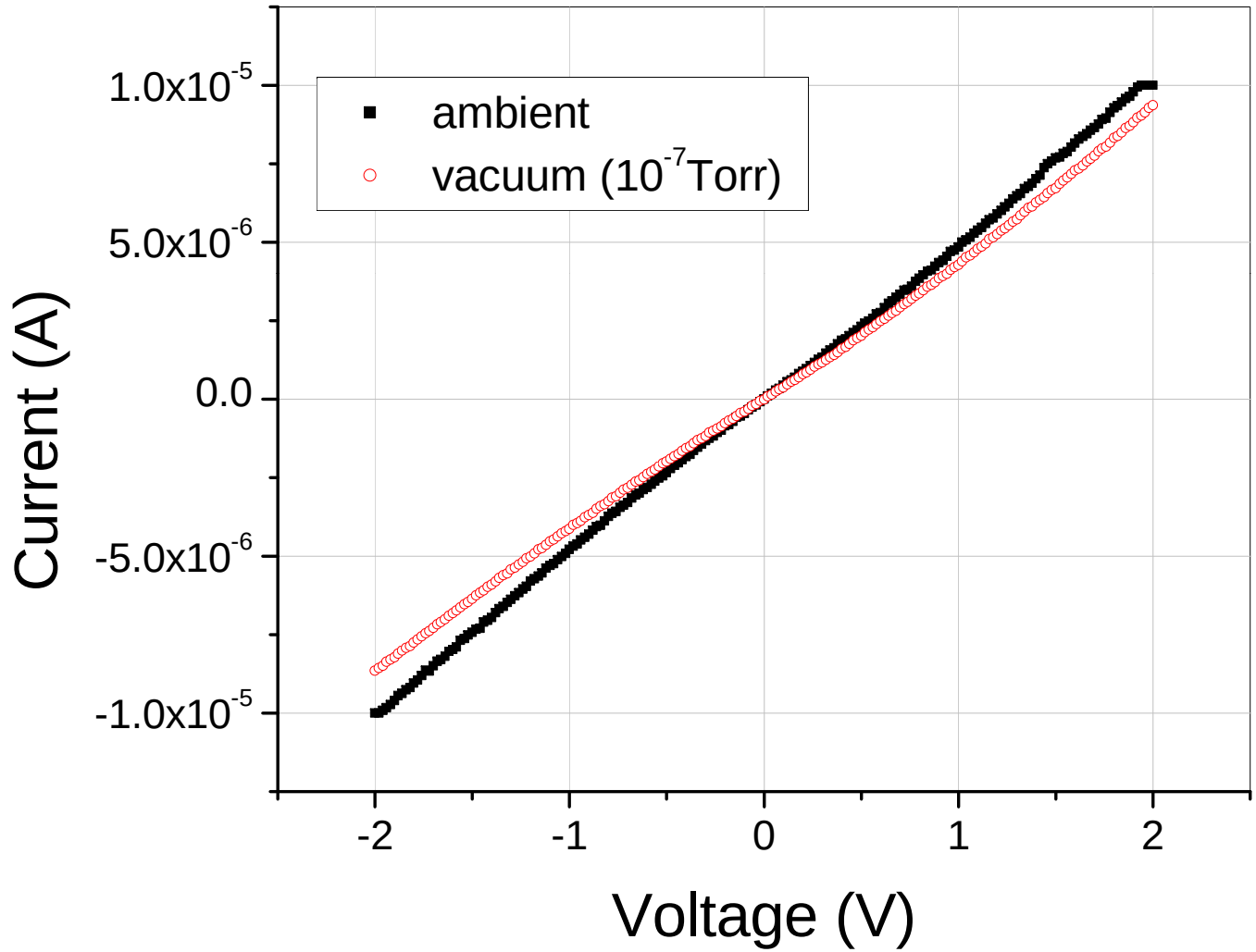


Wet Process Effects



Tube Chirality

Metallic tubes



Heat Dissipation

$$E_t = E_s + E_r + E_g$$

$$E_s = (K\Delta TA)/L$$

A = area through which heat transfer occurs,
K = thermal conductivity of the SiO2
ΔT = temperature difference between the current carrying element and the substrate
L = distance from the element to the substrate

$$E_r = \sigma\varepsilon(T_h^4 - T_a^4)A$$

σ = Stefan-Boltzmann radiation constant
ε = thermal emissivity of element
T_h, T_a = temperatures of the element and ambient

$$E_g = \alpha_r \Lambda_t AP(T_h - T_a)\sqrt{\frac{273}{T_h}}$$

α_r = accommodation coefficient
Λ_t = free molecule thermal conductivity
A = surface area of the element
P = pressure