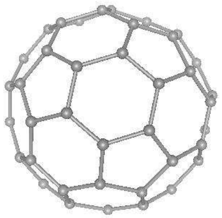


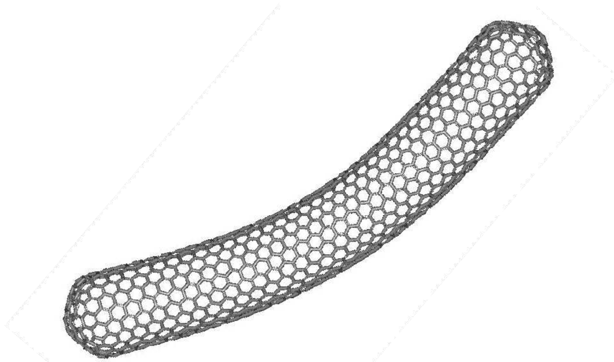
Carbon Nanomaterials Research at UVa

I. Core Capabilities

II. Nanotubes

III. Endohedral magnetofullerenes

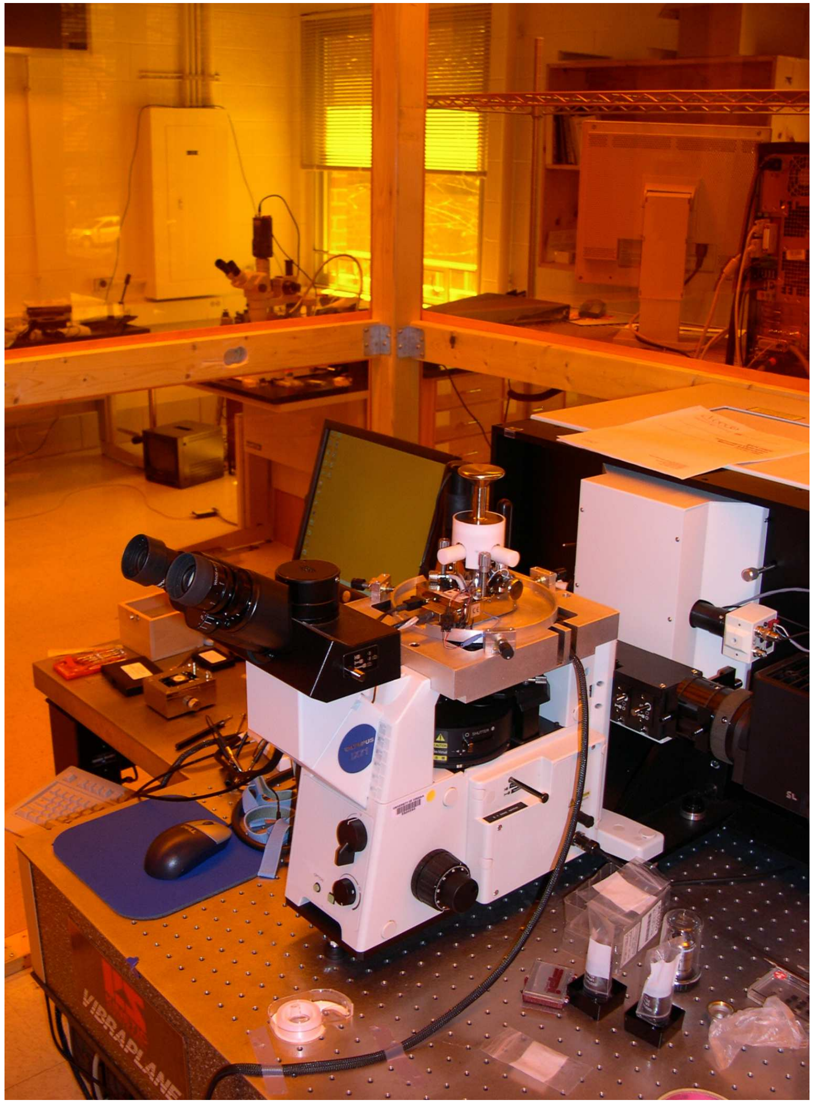
IV. Future Directions



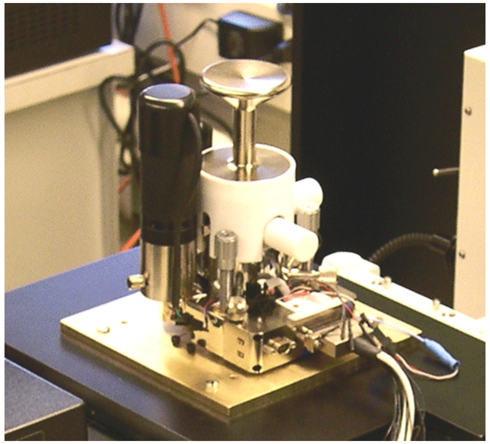
UVa, 23 October 2009

Electron Beam Lithography (~80 nm)

UV-vis-IR Micro-Raman Spectroscopy



Atomic Force Microscopy

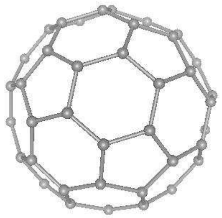


Optical Cryostat

…plus CVD nanotube growth, general wafer processing (UVML), and numerous light sources…

Core experimental collaborations…

- Oak Ridge CNMS (high-res Raman etc.)
- VT Chemistry (magnetofullerenes)
- Luna Corp. (193 nm superlenses; trimetaspheres)
- NIST & Argonne (growth of epitaxial graphene; IETS)



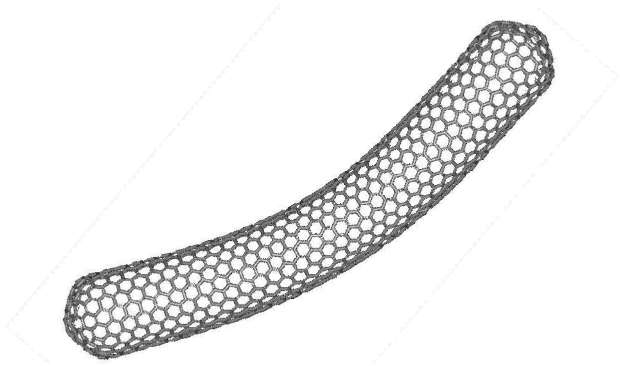
Carbon Nanomaterials Research at UVa

I. **Core Capabilities**

II. **Nanotubes**

III. **Endohedral magnetofullerenes**

IV. **Future Directions**



UVa, 23 October 2009

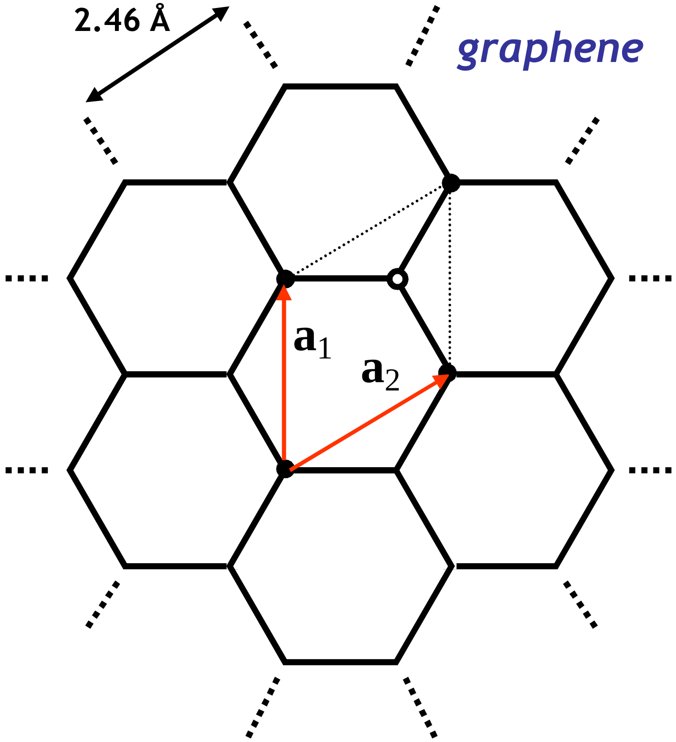
Quick Review of Single-walled Carbon Nanotubes…

- Electronic structure closely related to that of *graphene*.

- Tight-binding: consider only nearest-neighbor wavefunction overlap.

- Let γ_o be the overlap integral between the neighboring atoms

  $\rightarrow$2D dispersion of graphene[‡] :



$$E(k_x,k_y) = \pm\gamma_0\sqrt{1+4\cos\left(\frac{\sqrt{3}k_xa}{2}\right)\cos\left(\frac{k_ya}{2}\right)+4\cos^2\left(\frac{k_ya}{2}\right)}$$

References

[‡] P.R. Wallace, *Phys. Rev. Lett.* **71**(9) 622-634, 1947

SWNT as molecular interconnects:

- Cylindrical boundary conditions define a tube:

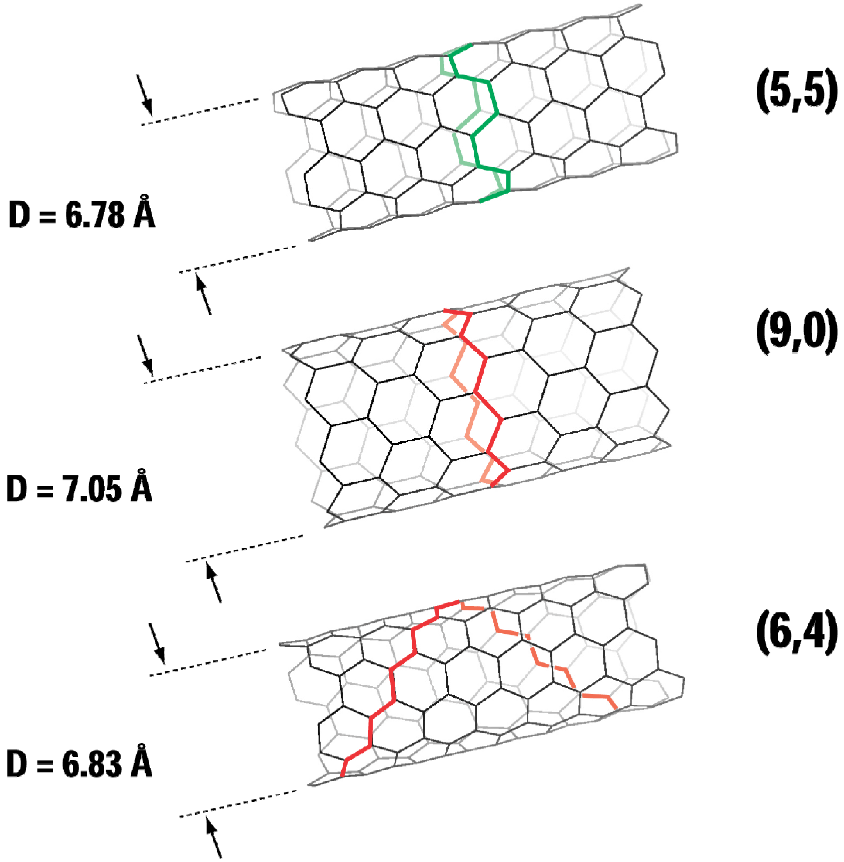
$$\mathbf{C} = n\mathbf{a}_1 + m\mathbf{a}_2$$

- Chiral indices (n,m) determine the band structure[‡]:

|n-m| = 0,3,6,... , *metallic*;

otherwise *semiconducting*.

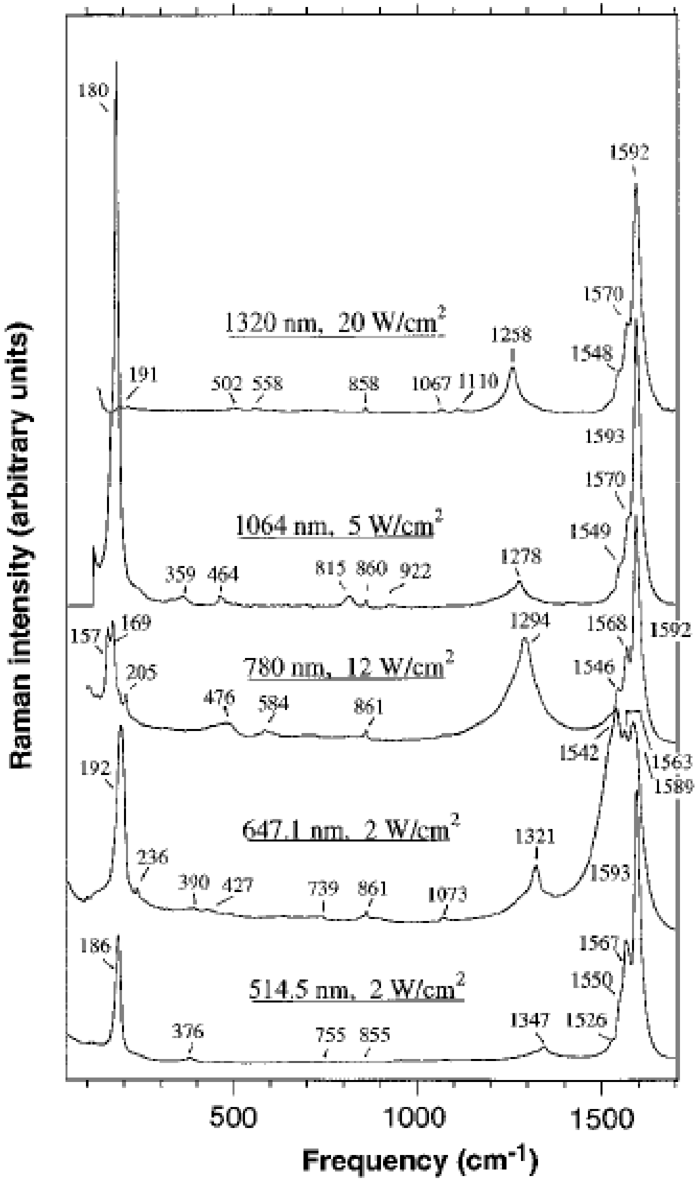
(valid for all but the smallest diameter nanotubes)

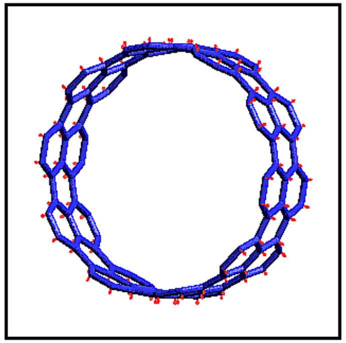


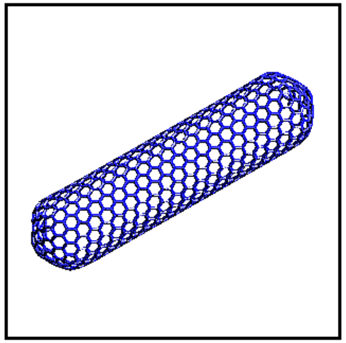
Reference

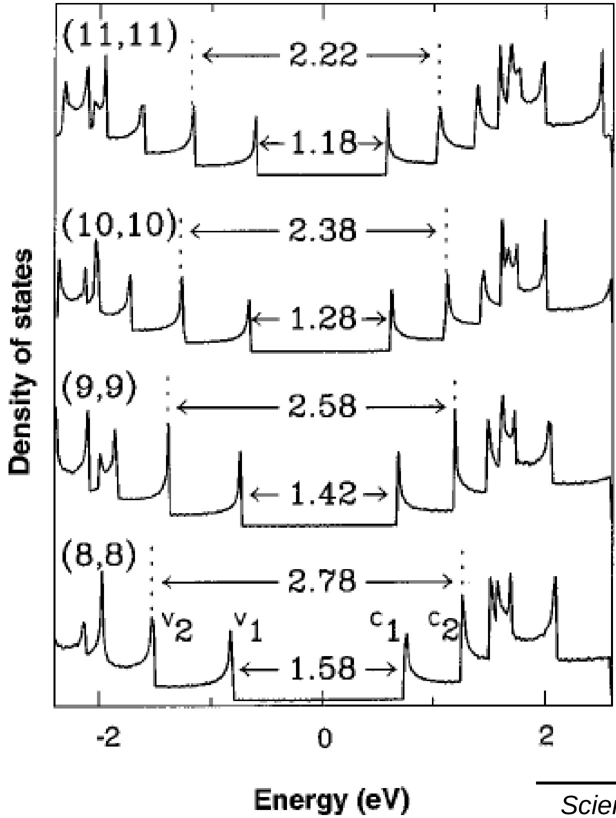
‡ J.W. Mintmire et al., *J. Phys. Chem. Sol.* **54**(12) 1835-1840, 1993.

Nanotube Resonant Raman



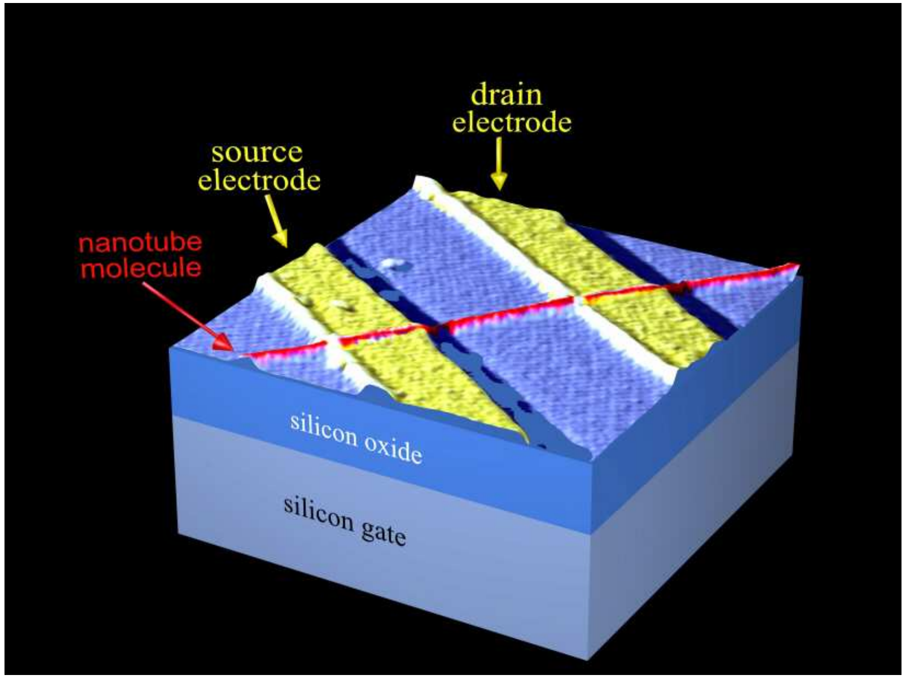






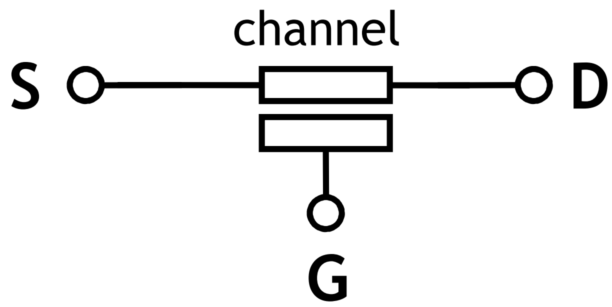
Science **275** (1997)

Nanotube-based FETs…

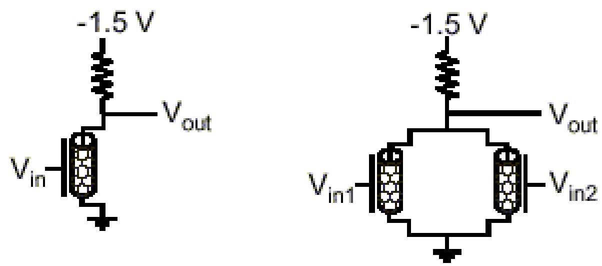


- Channel = semiconducting nanotube
- FETs can also be gated by a local wire or by a liquid
- Smallest tubeFET ~100 nm (gap between source and drain)
- Top-down FET logic gates have been made

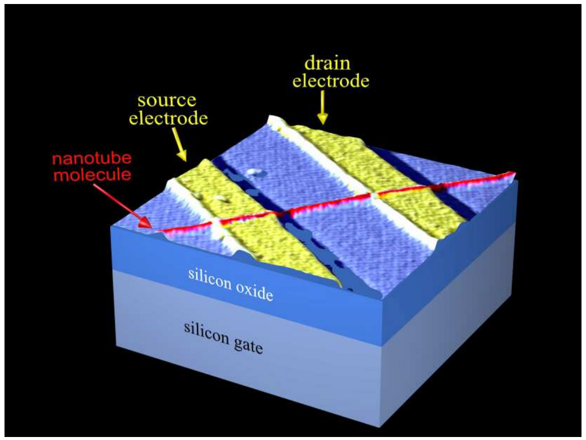
FET Structure:

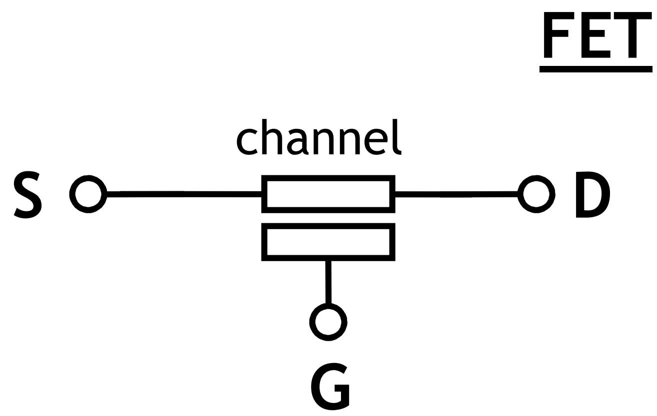


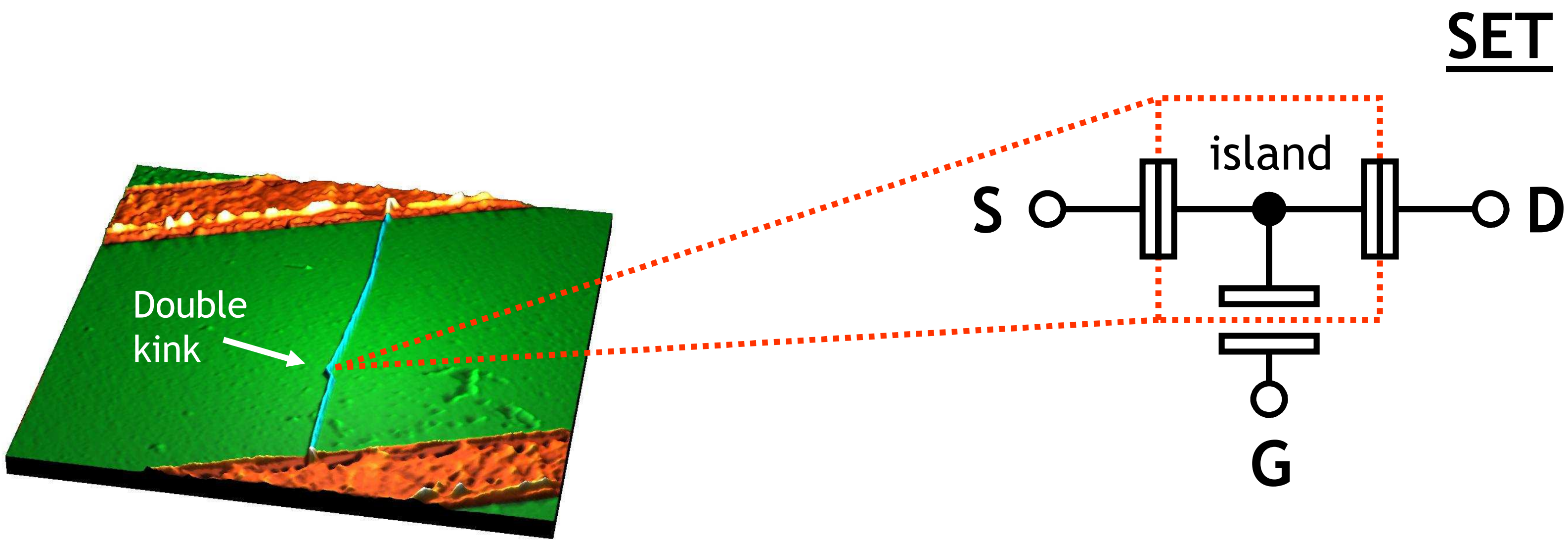
Tube-FET Logic (Bachtold, Delft)



Room-temp. SETs also possible…

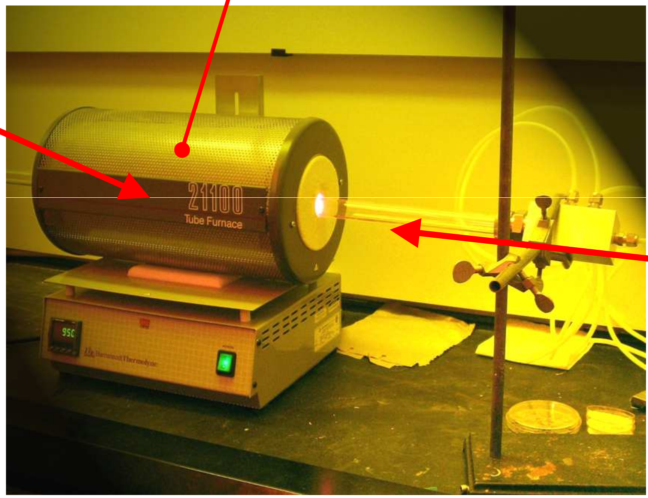






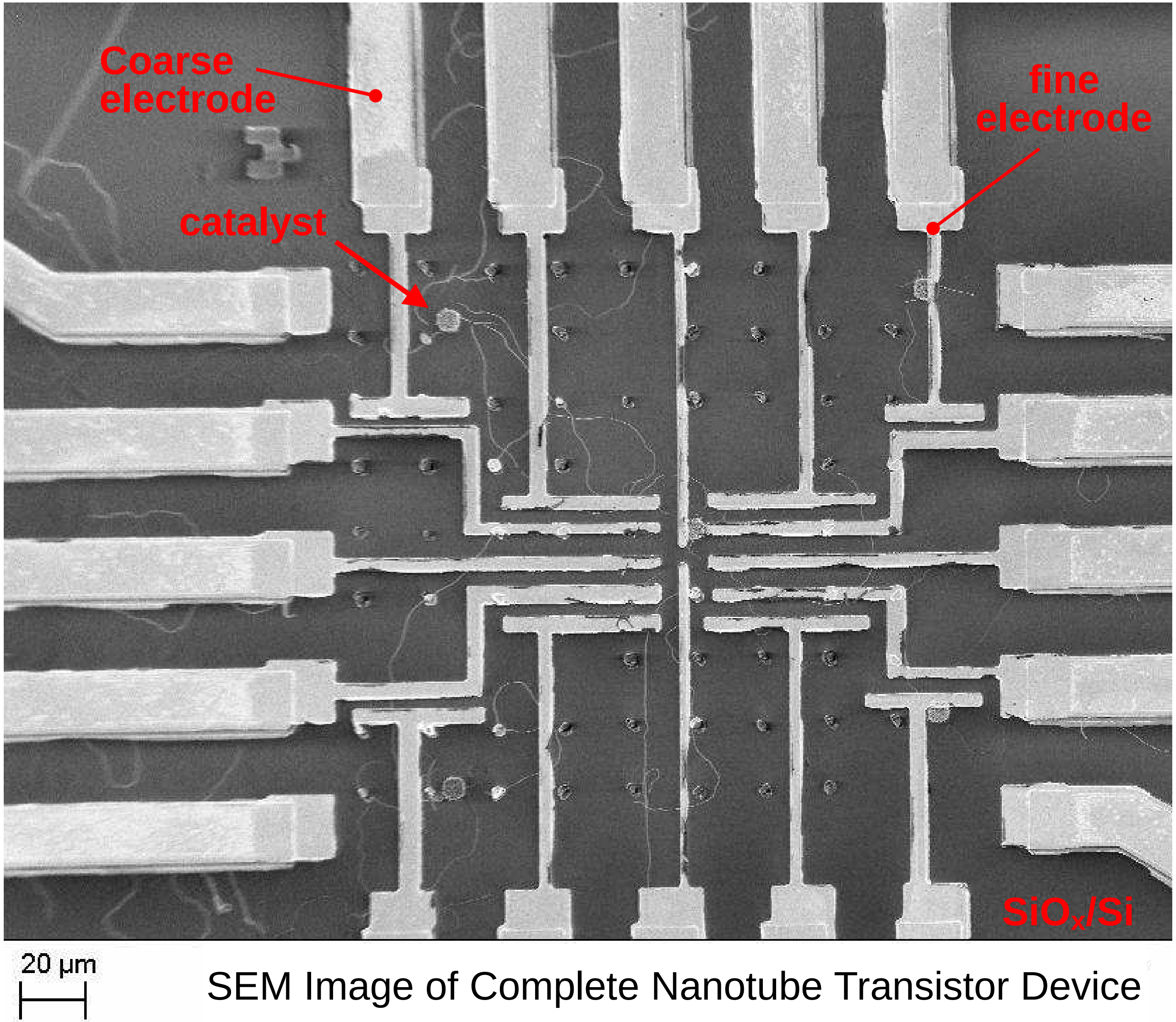
(Postma, Delft)

Chemical Vapour Deposition Growth of Nanotubes



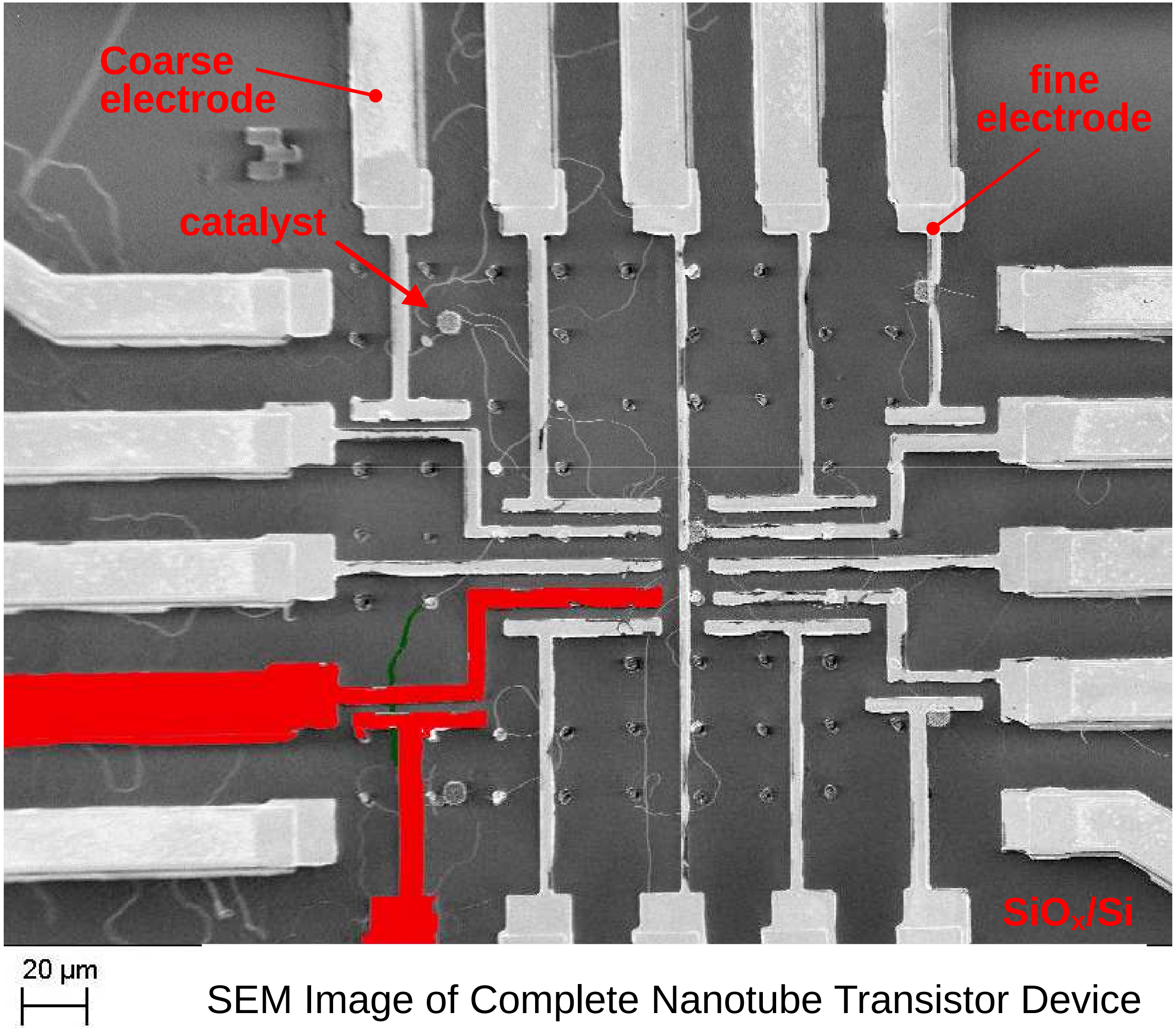
Catalyst deposition
↓
Nanotube growth
↓
SEM
↓
E-beam lithography
↓
Transport, Raman etc.

N.b. one of the ‘hands on’ labs for my PHYS 582 nano class...



SEM Image of Complete Nanotube Transistor Device

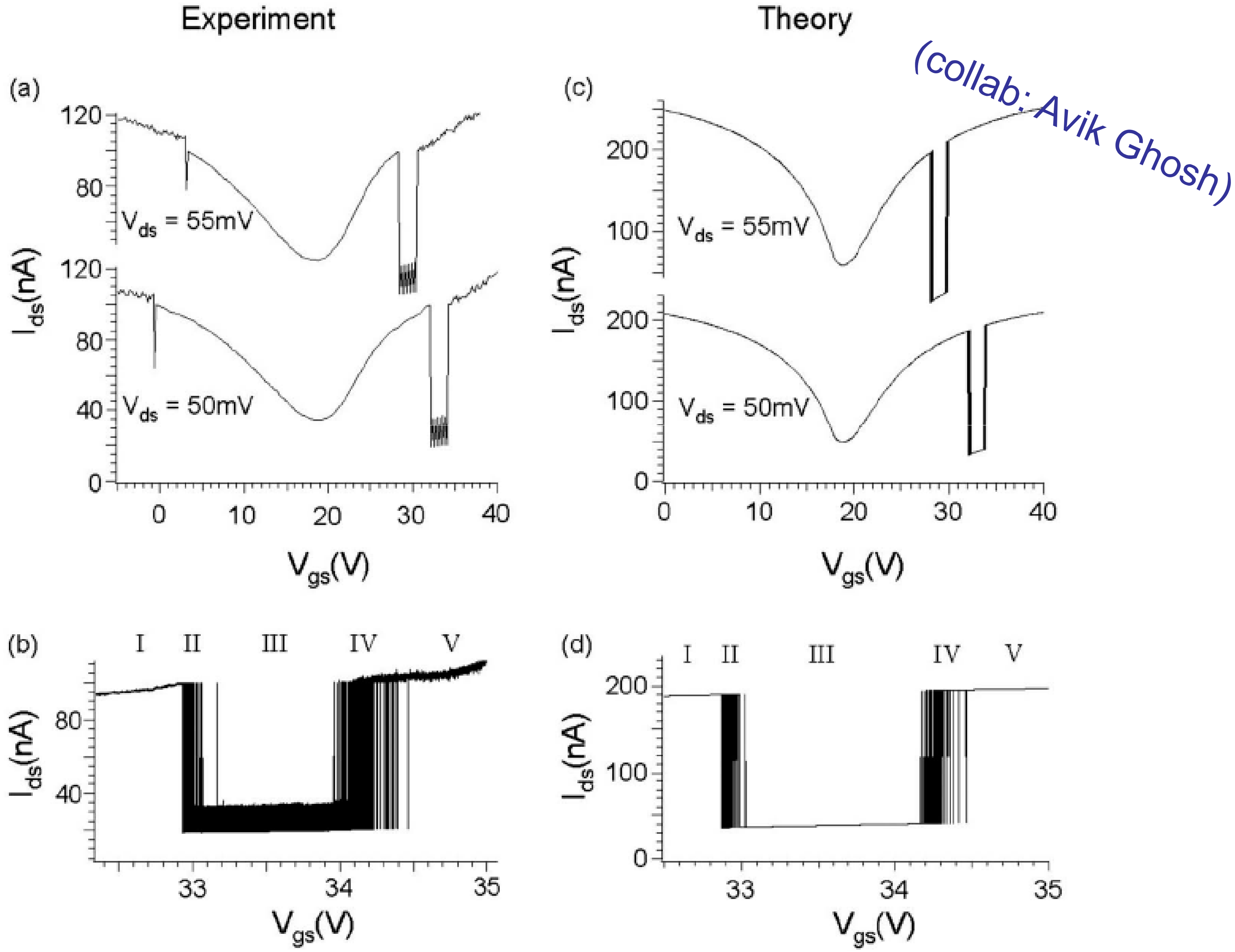
Catalyst deposition
↓
Nanotube growth
↓
SEM
↓
E-beam lithography
↓
Transport, Raman etc.



SEM Image of Complete Nanotube Transistor Device

Catalyst deposition
↓
Nanotube growth
↓
SEM
↓
E-beam lithography
↓
Transport, Raman etc.

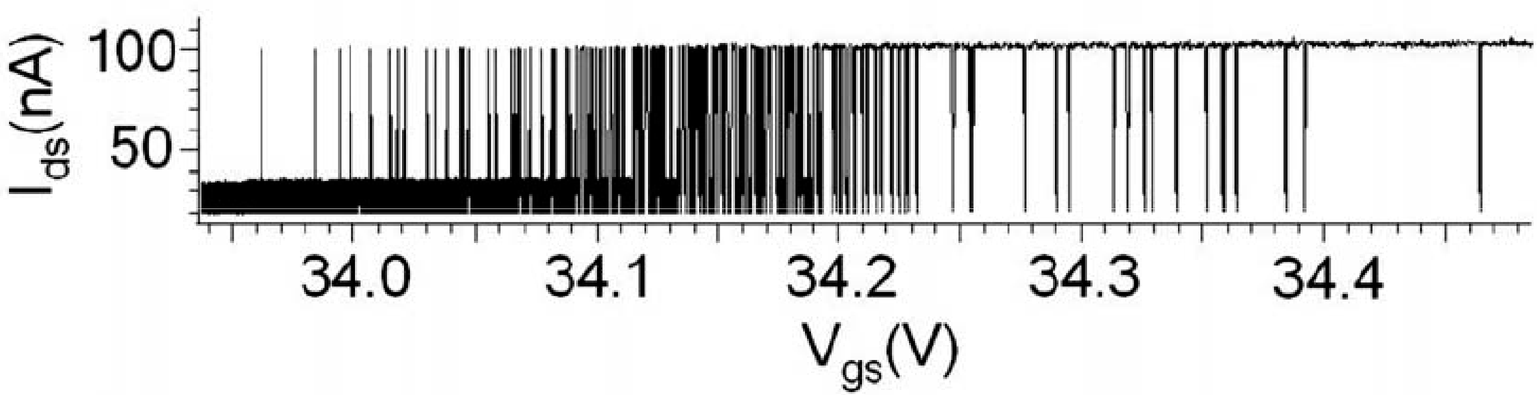
Reversal of current blockade in nanotube-based FETs through multiple trap correlations … at room temperature



-Chan et al. PRB (2009)

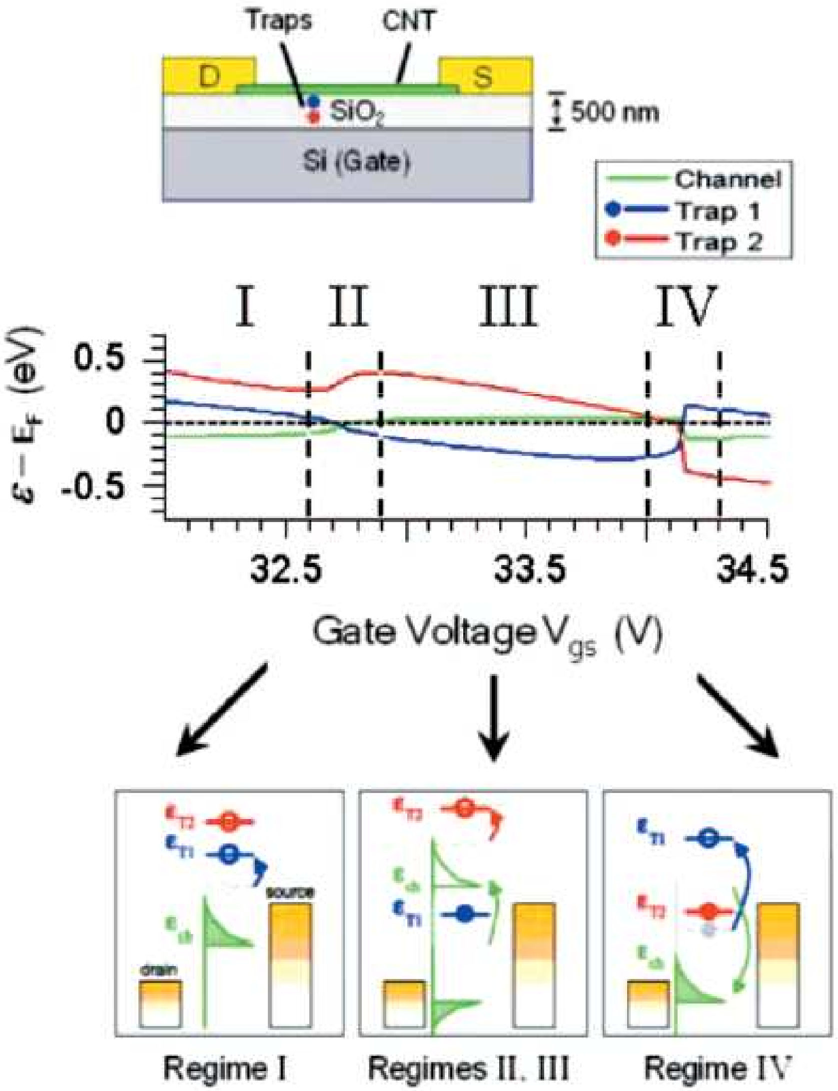
Reversal of current blockade in nanotube-based FETs through multiple trap correlations

Stochastic switching between two levels….



… RTS amplitude reaches 80% of current, at room temperature!

Reversal of current blockade in nanotube-based FETs through multiple trap correlations



"trap juggling"

Reversal of current blockade in nanotube-based FETs through multiple trap correlations

Key points:

- Observed in long-channel nanotube FETs
- unprecedentedly high amplitude, at room temperature
- multiple traps with correlated electrostatics
- 1D channel → <u>very</u> sensitive to gate, thus can resolve closely adjacent traps

…and noisy current through nanotubes isn't so unusual; why?

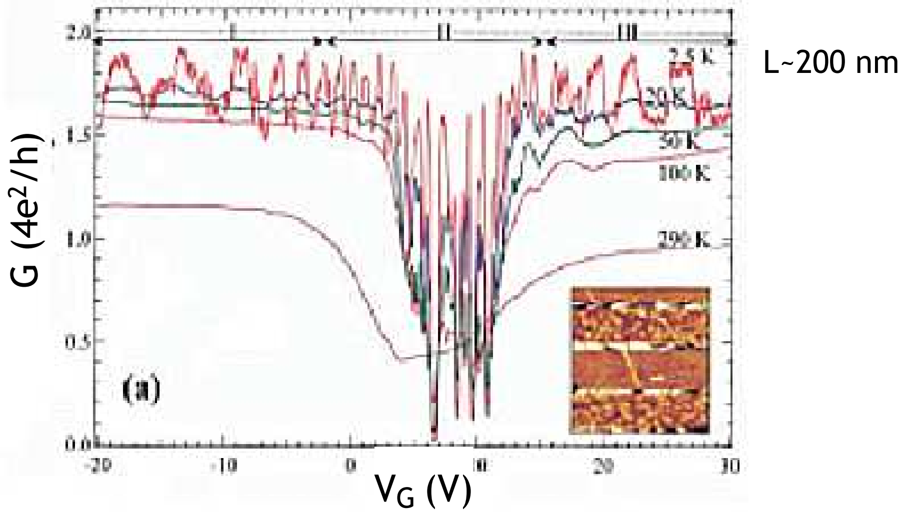
Nanotube transport:

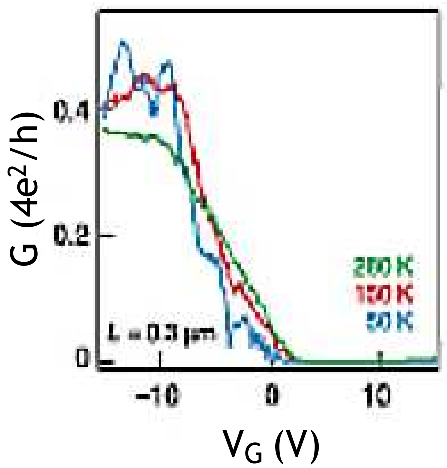
- 1D, ballistic conductance observed
- 2 transport channels
- Contacts are important!

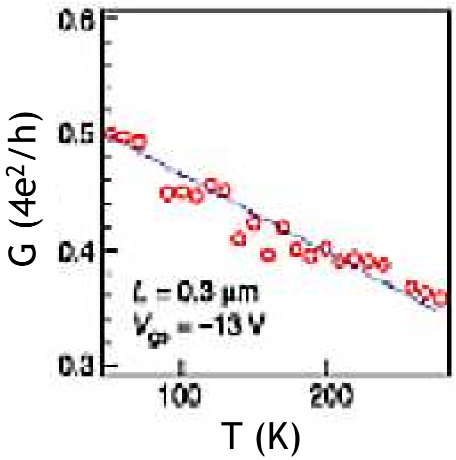
<u>Metallic SWNT</u>[†] : Ti contacts
$G \approx 2G_0$

<u>Semiconductors</u> [‡] : Pd contacts
$G \approx 0.5G_0$

$$G = \frac{2e^2}{h} \sum_{channels} T_i = \frac{4e^2}{h}$$



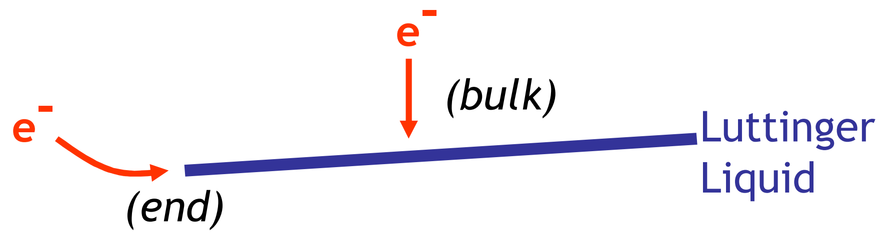




References

† Kong & Dai et al., *Phys. Rev. Lett.* **87**(10) 106801, 2001.
‡ Javey & Dai et al., *Nature* **424** 654, 2003.

Nanotube transport:



- 1D Tomonaga/Luttinger[†] liquid behavior is anticipated:

$$G \propto T^{\alpha}$$

$$\rho(E) \propto |E|^{\alpha}$$

$$\alpha_{end} = (g^{-1} - 1)/4$$

$$\alpha_{bulk} = (g^{-1} + g - 2)/8$$

$$0 \le g \le 1$$

g=1 for zero long-range Coulomb interaction (non-correlated electrons)

g<1 for long-range, repulsive Coulomb interactions

- Observations of *LL* behavior in SWNT:

Bockrath, transport studies:
α ~ 0.3

Yao & Postma, intramolecular junction:
g ~ 0.22

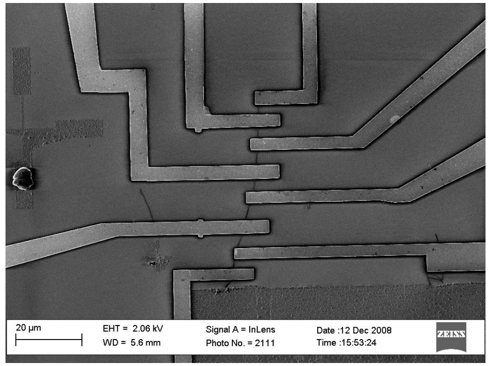
Ishii, photoemission studies, on Au:
g ~ 0.18

References

† Tomonaga, S., *Prog. Theor. Phys.* **5** 544 (1950); Luttinger, J.M., *J. Math. Phys.* **4** 1154 (1963).

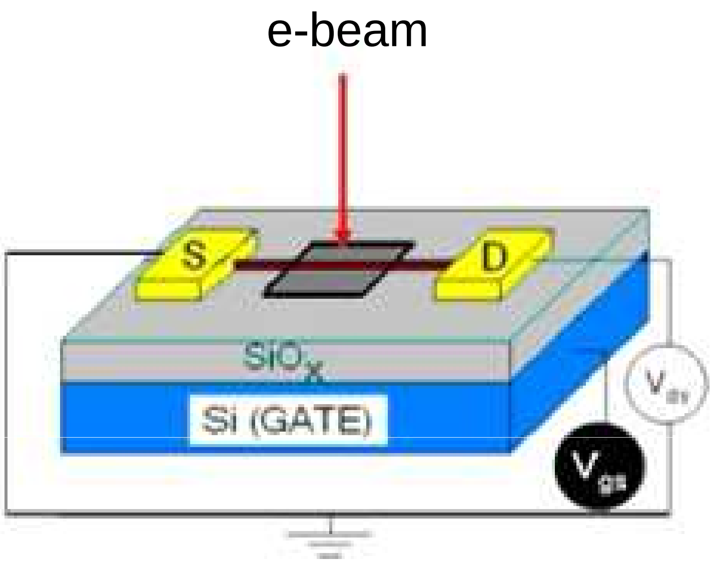
EBL with in situ transport measurement…

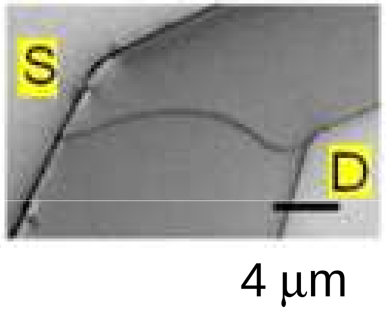
source
drain
gate



…and attach gas cylinders to vent chamber to O_2, H_2, etc.

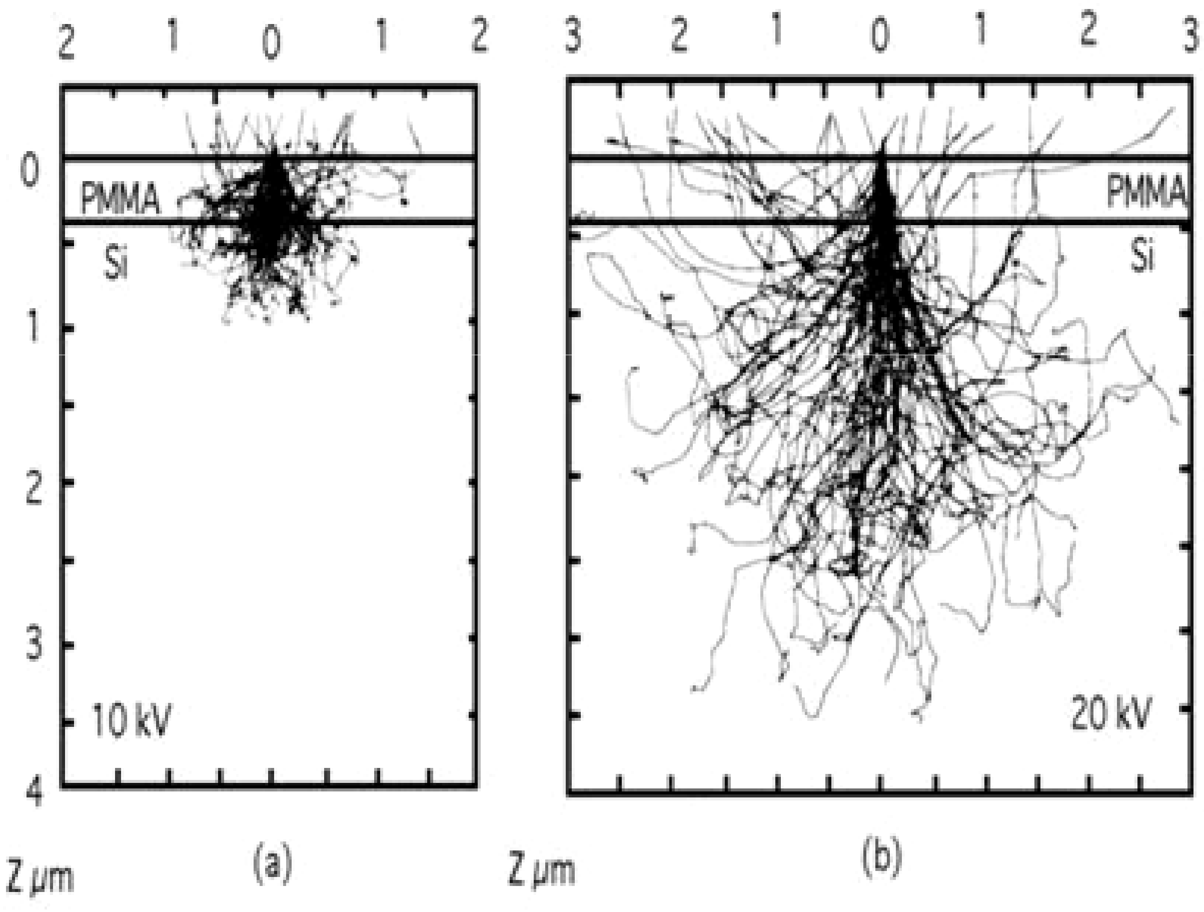
…this allows us to write *across* contacted nanotubes and look for current noise generated by surface charging and/or beam damage…





…a portion of the tube channel is exposed to e-beam after the FET device is completed…

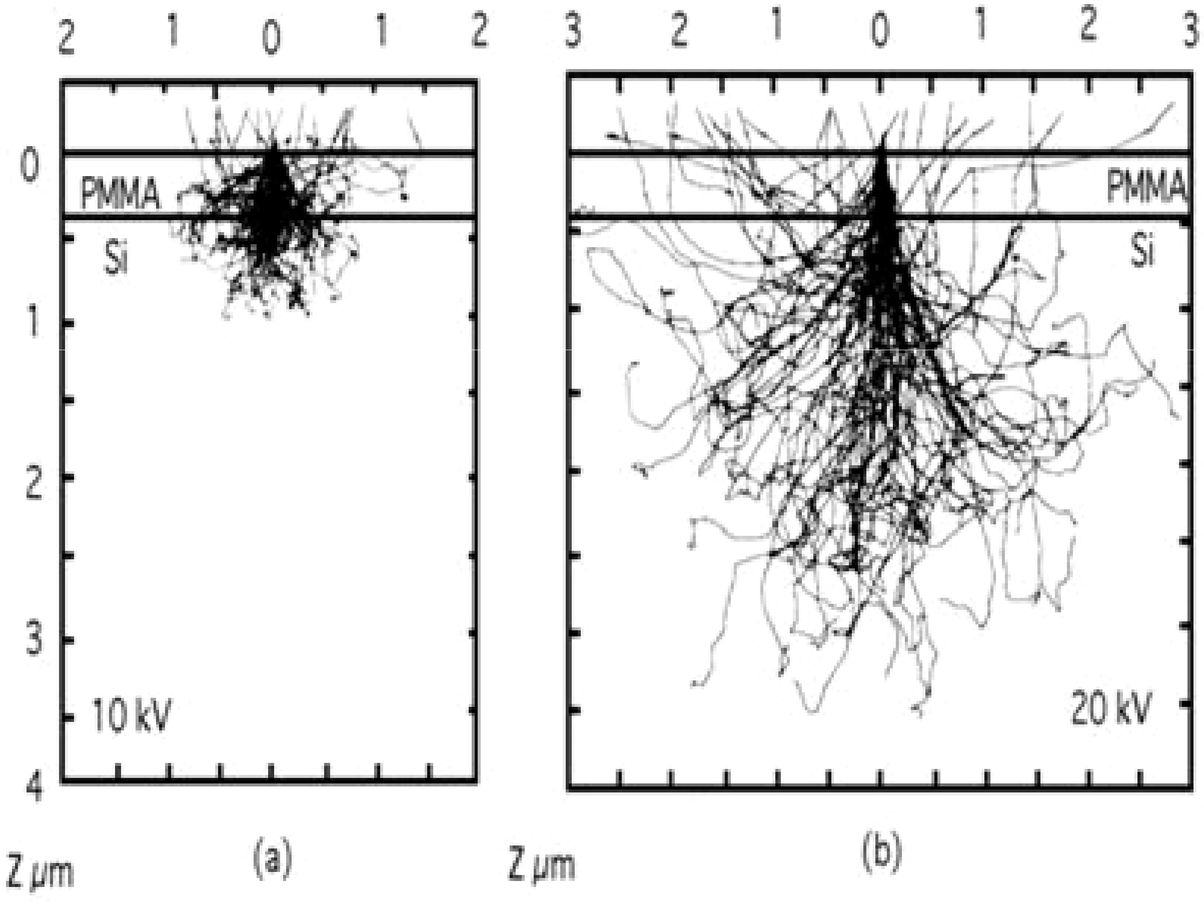
Recall scatter / backscatter / proximity issues with e-beam lithography:



-Monte Carlo Simulation, http://cmi.epfl.ch/ebeam

Recall scatter / backscatter / proximity issues with e-beam lithography:

(responsible for 'undercut' seen in resist)



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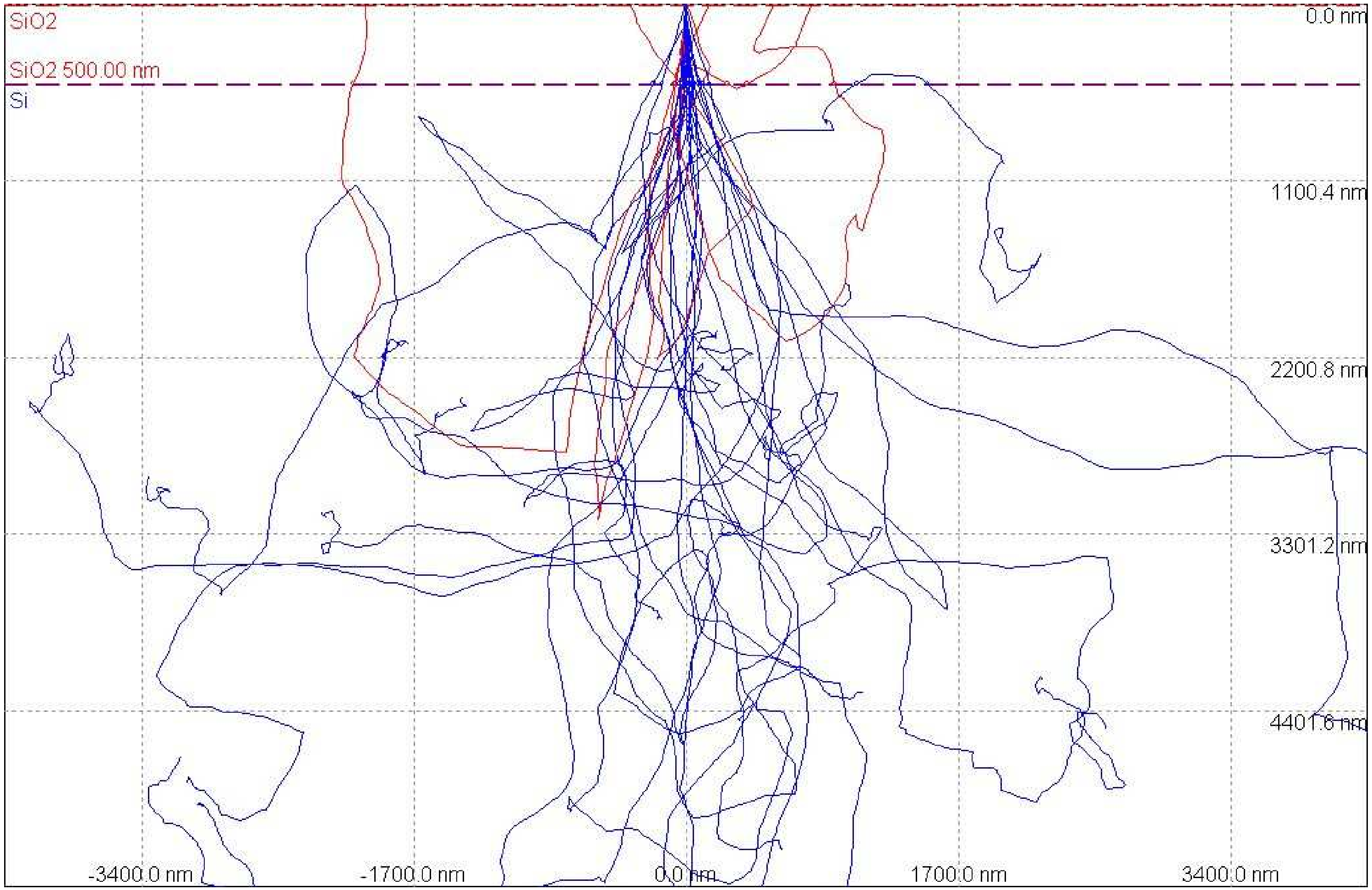
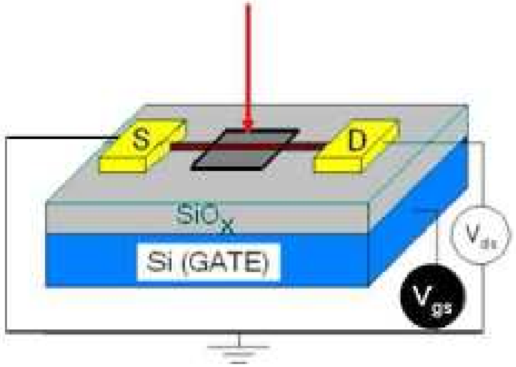
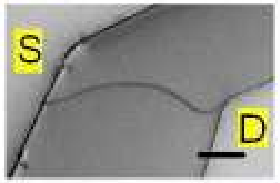
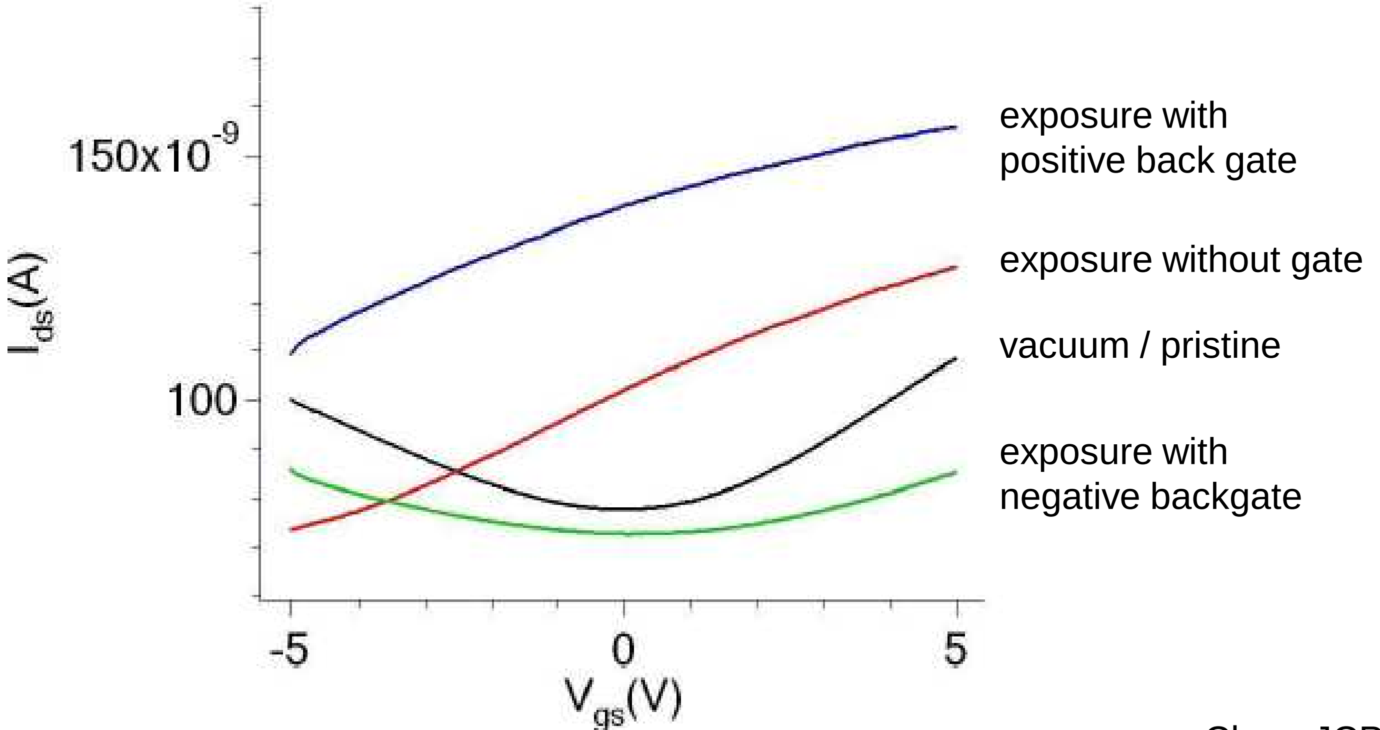


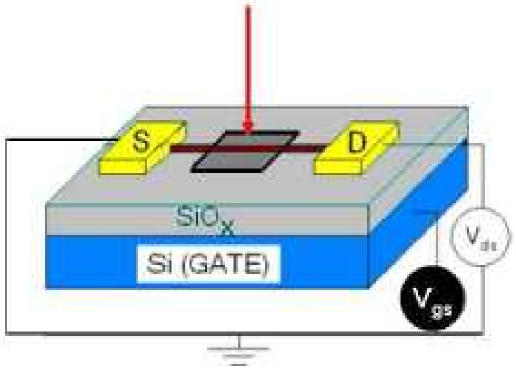
From Casino, 30kV

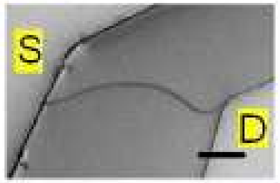




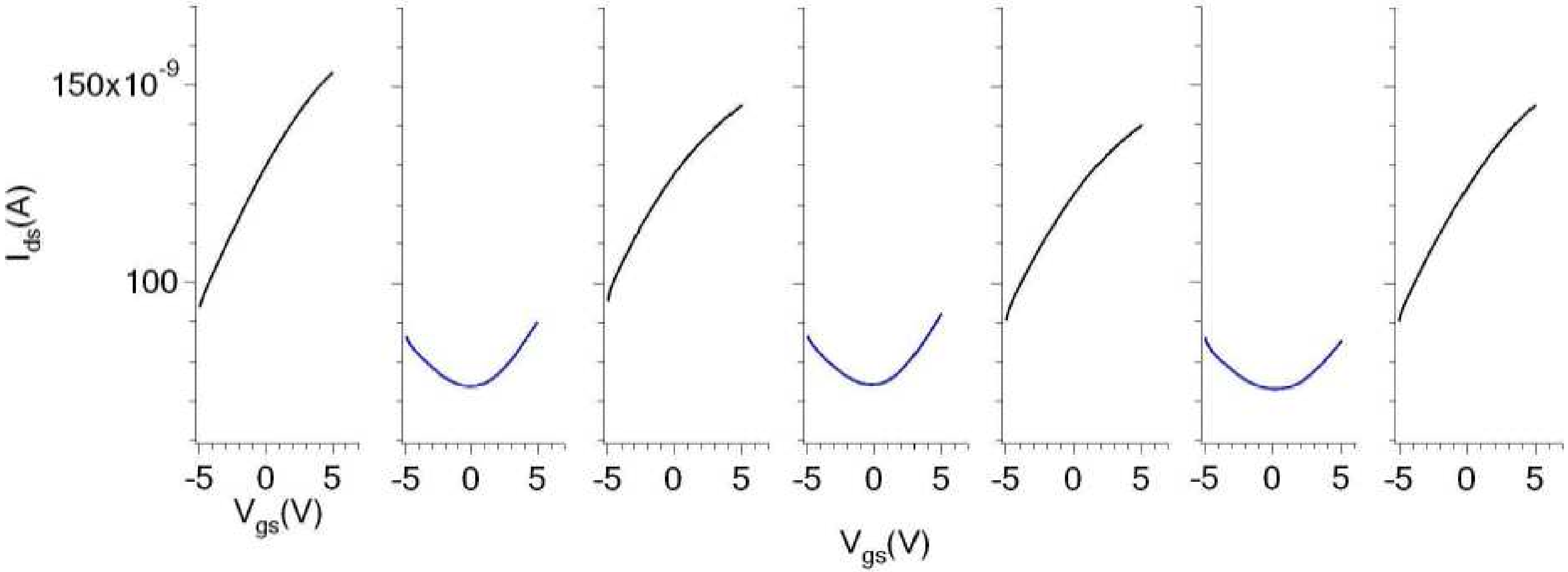


-Chan, JCP (2009)

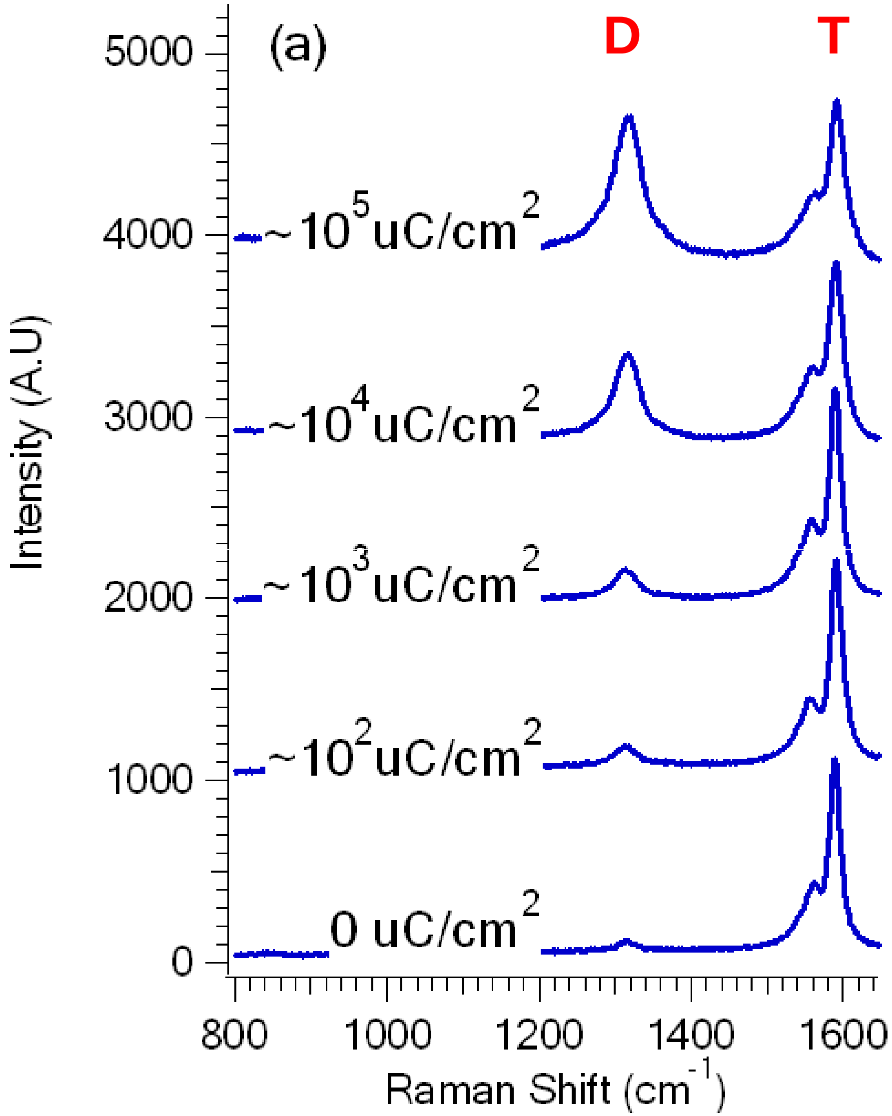




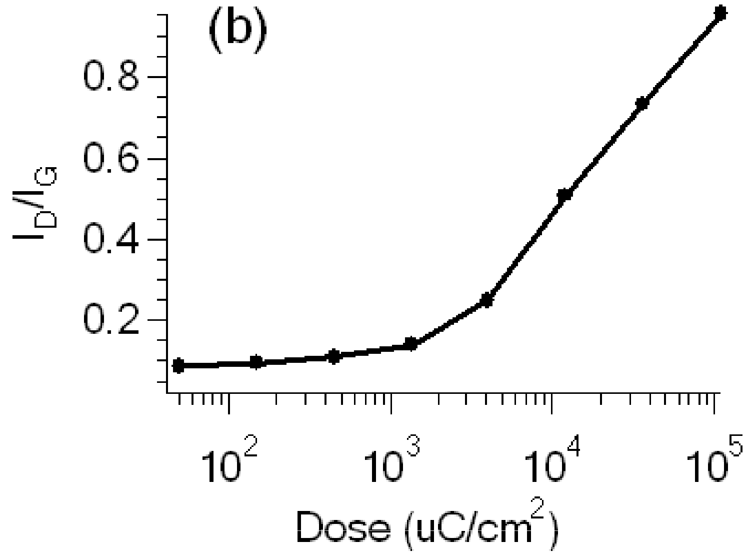
Transport after exposure with …+ gate …- gate …+ gate …- gate …+ gate … - gate …+ gate…



Raman disorder band reveals beam damage to the nanotube…

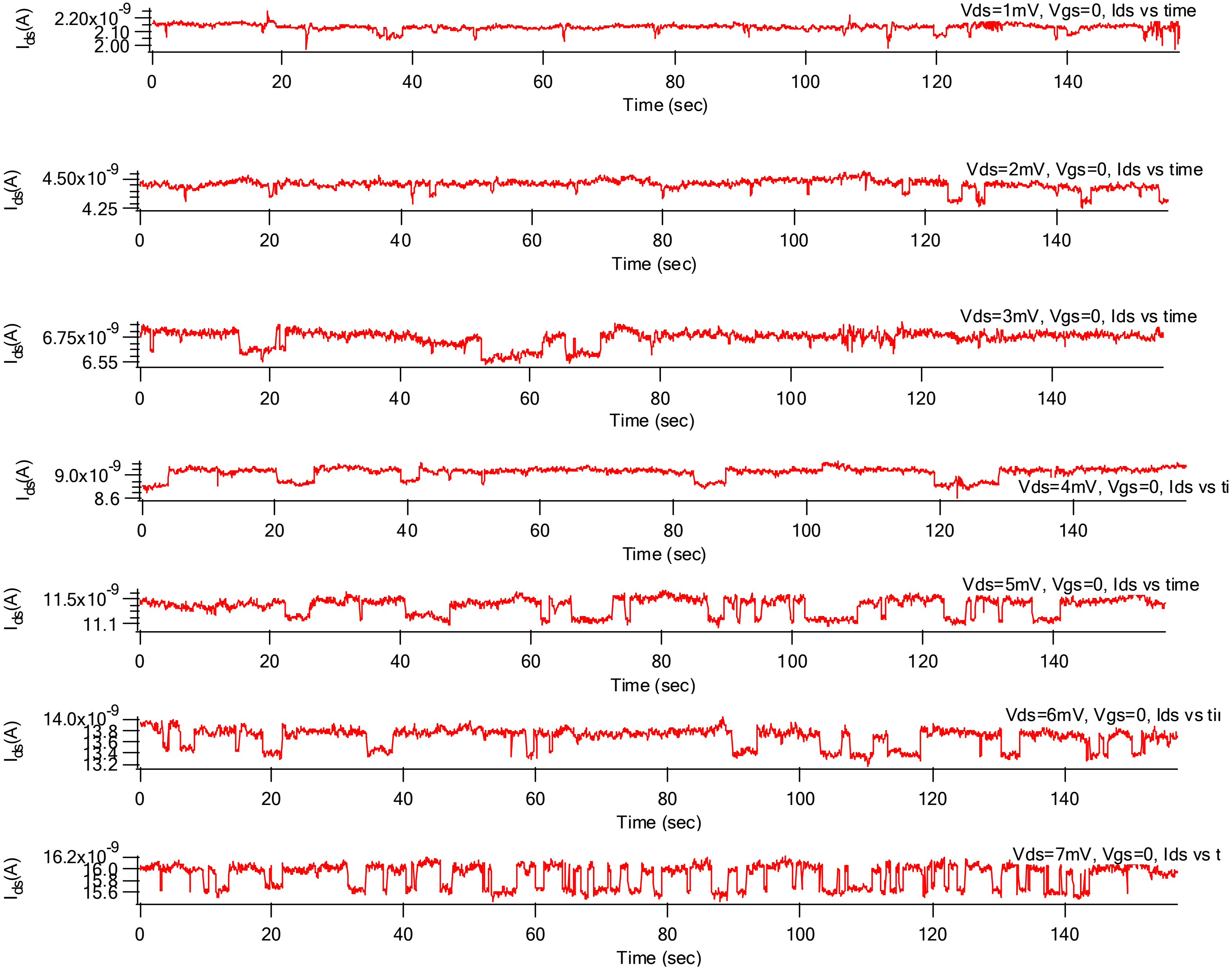


(N.b. data vertically offset)



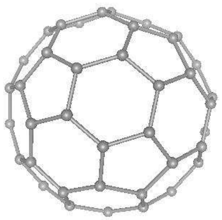
- Raman spectra of CNTs irradiated by e-beam with different doses
- D-band is induced by e-beam
- Electron energy =15 kV; beam current = 200 pA

…persistent noise induced by e-beam exposure….



Key points:

- possible to sever tubes with fairly low energy e-beam
- charge trapping observed → two-state current flicker
- substrate charging may contribute overall shift in ambipolar curve; this effect is related to backgate bas during exposure
- fine-scale writing of traps and tunnel barriers may be possible; multiply-segmented tubes currently being explored



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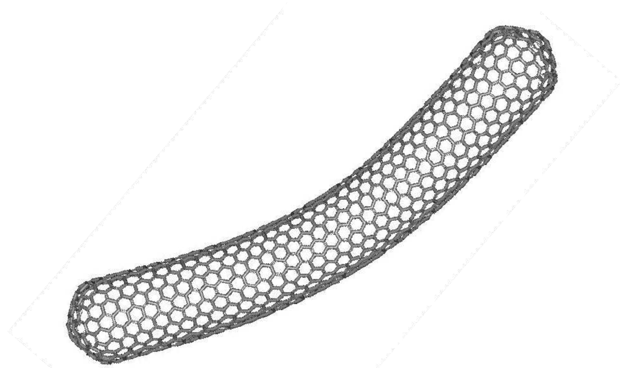
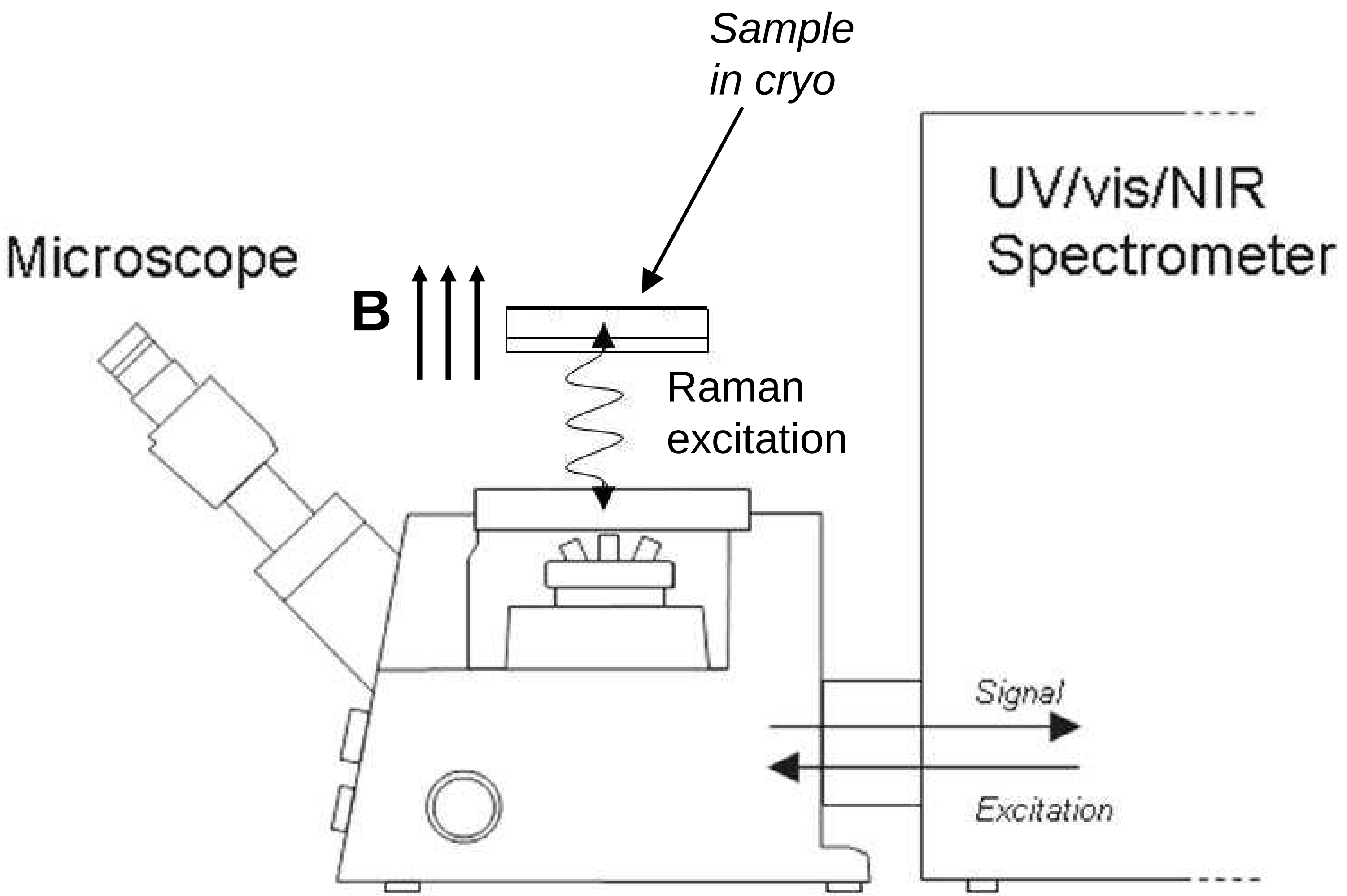
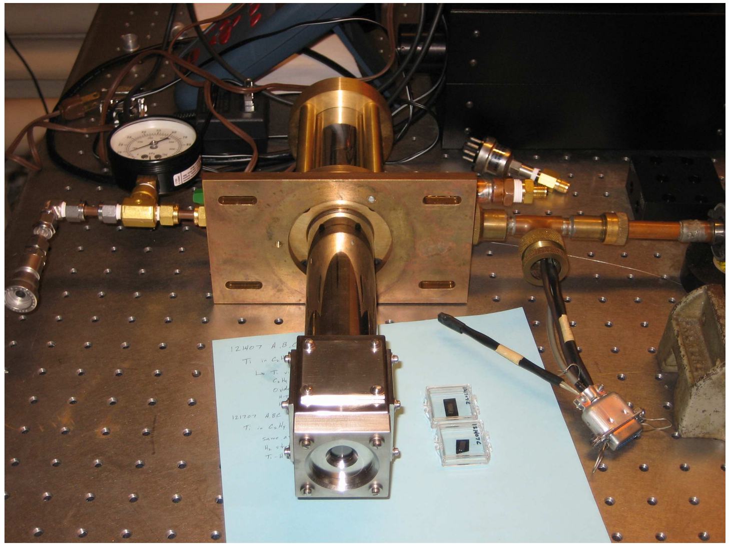


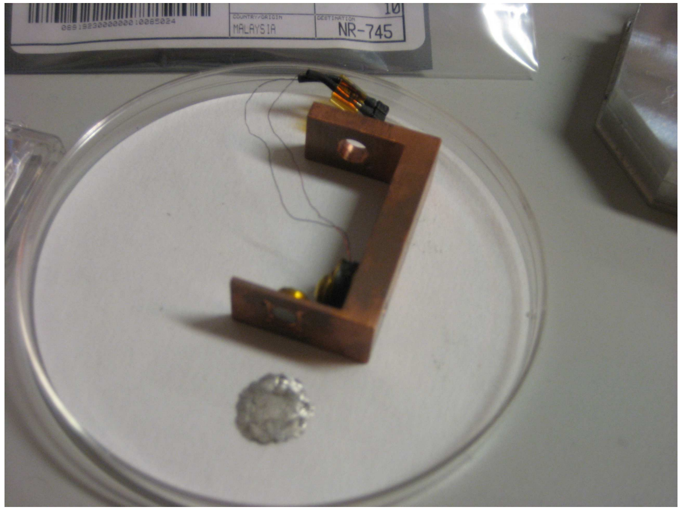
UVa, 22 October 2009

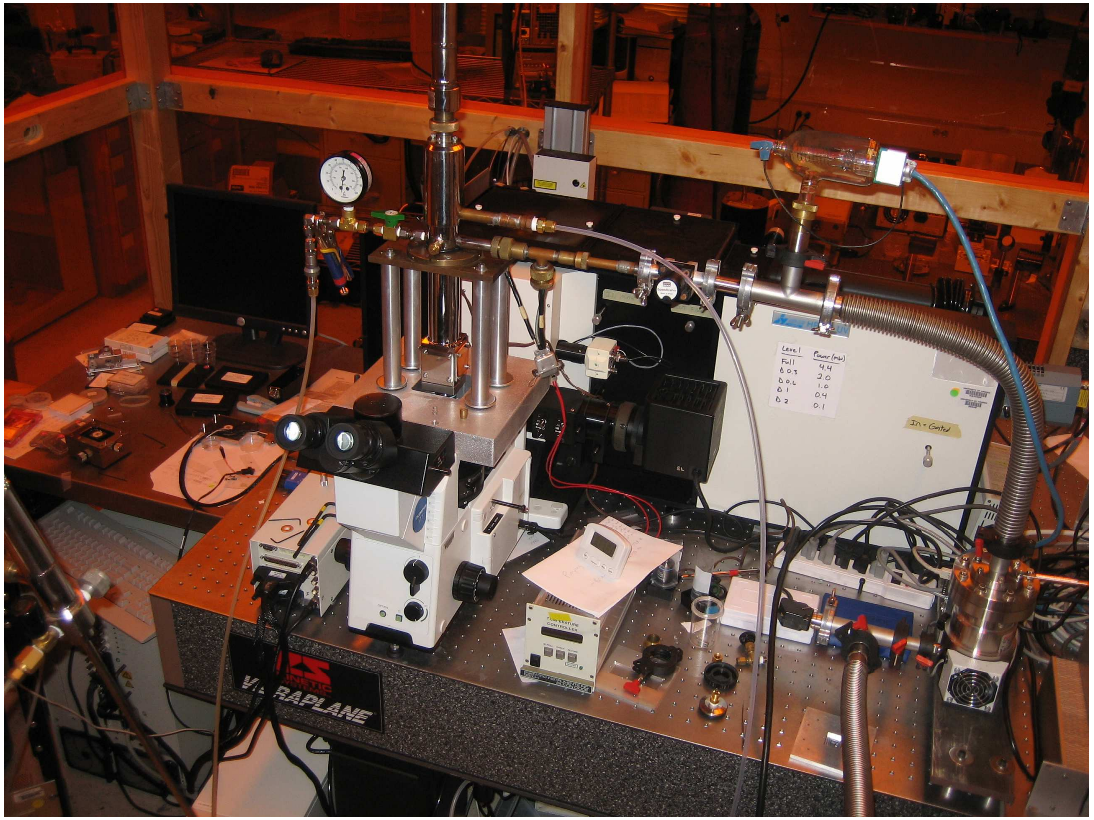
Magneto-Raman Apparatus
(completed Fall 2009)



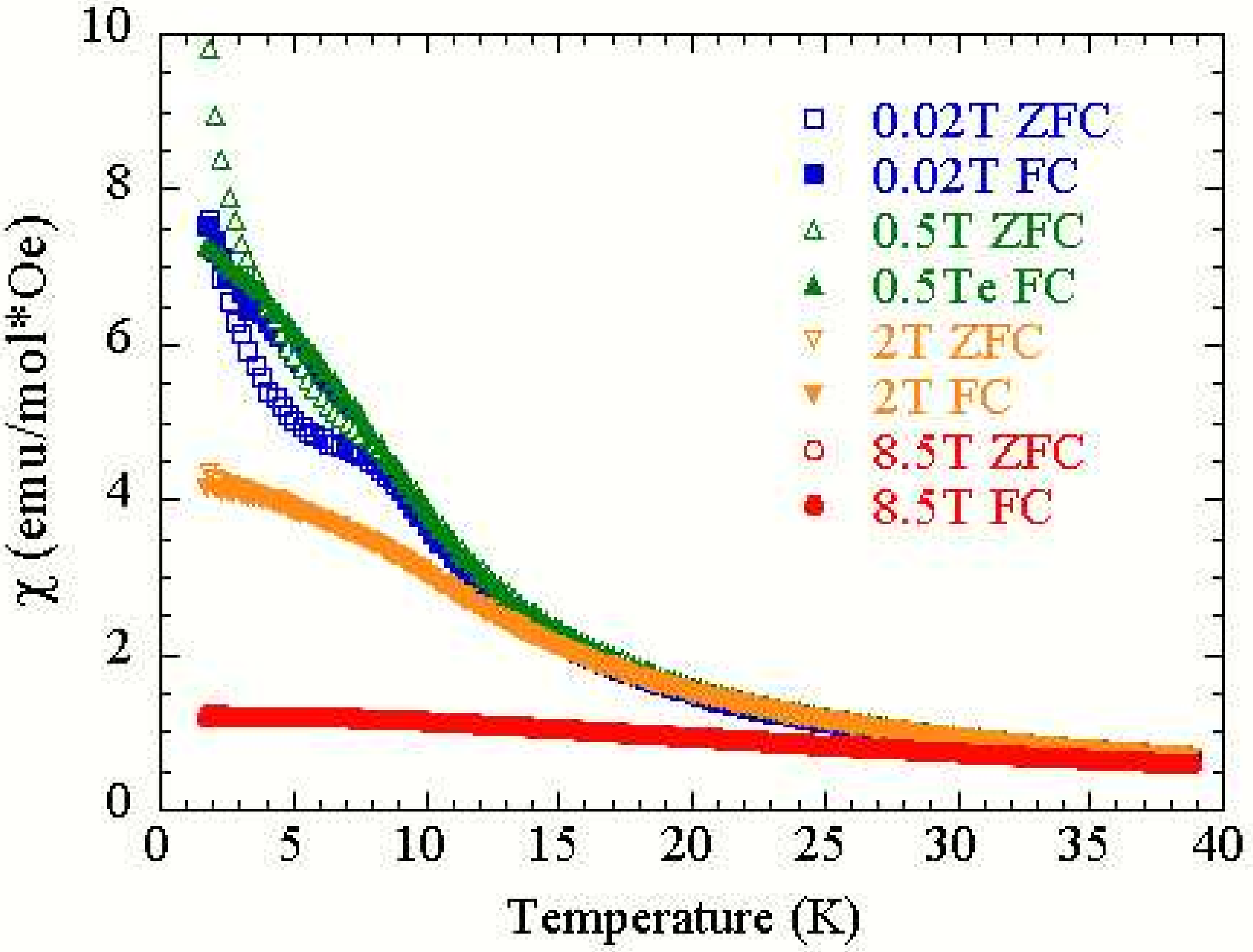
Previous work: Modified Optical Cryostat (10.2 – 300 K)





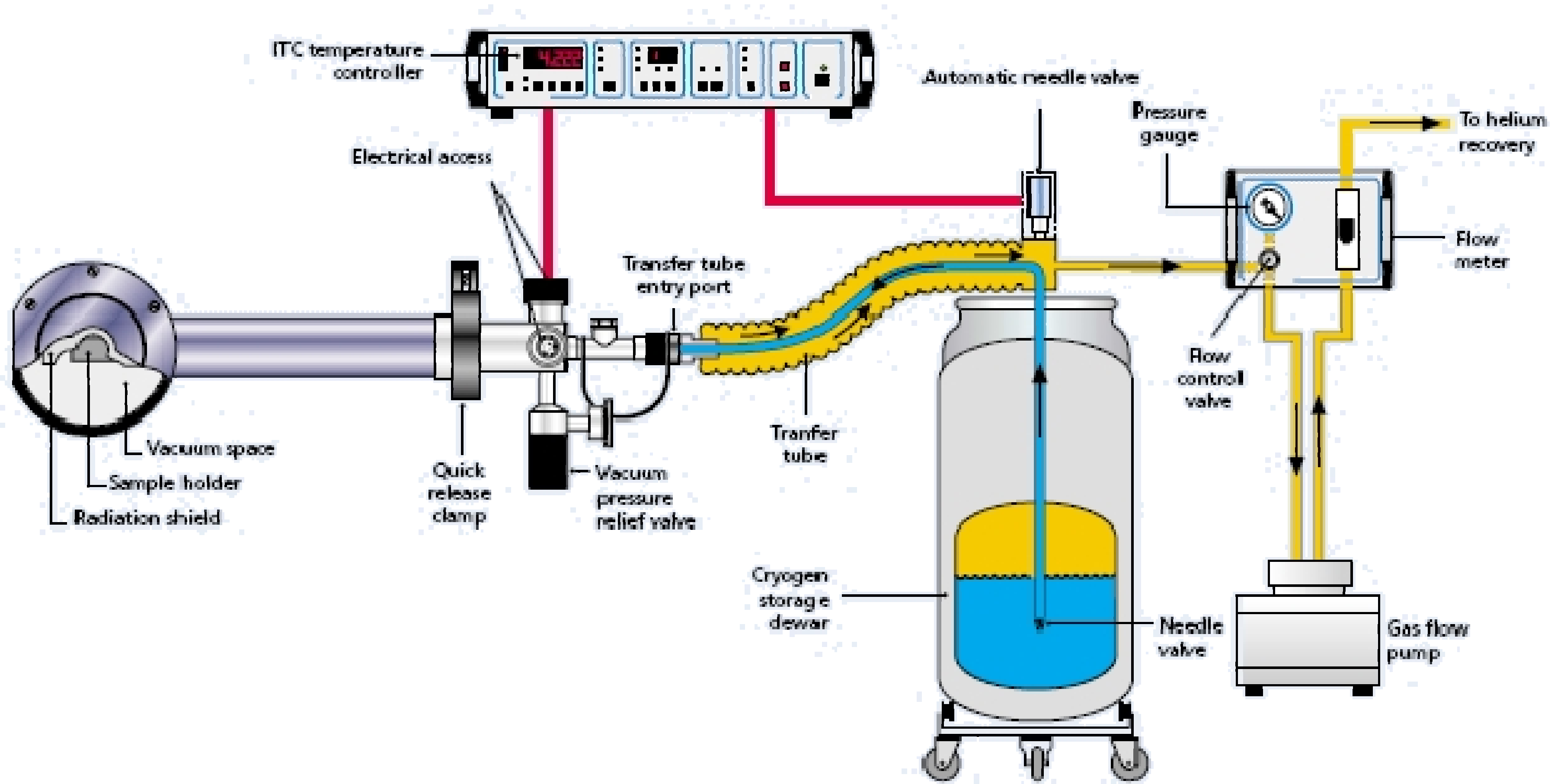


Susceptibility data shows inflection in $Gd_3N@C_{80}$



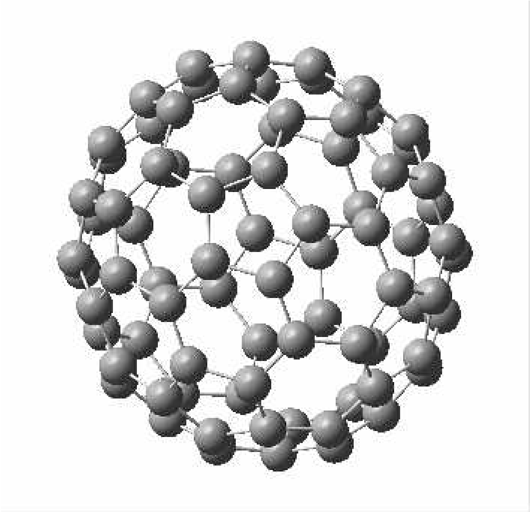
-Measured in Despina Louca's lab at UVa

Optical cryostat delivered Fall '09…

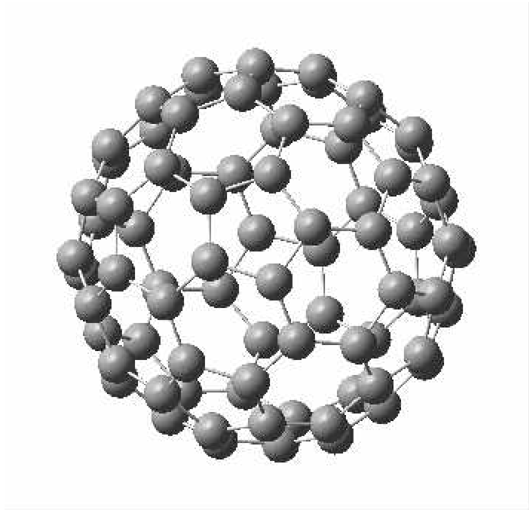


… permits micro-Raman + transport in a B-field at ~2K
… DARPA subcontract via Luna Corp.

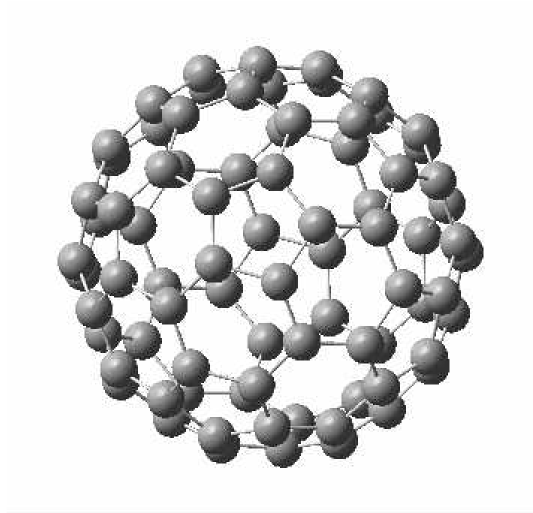
C_{80} Cage Modes



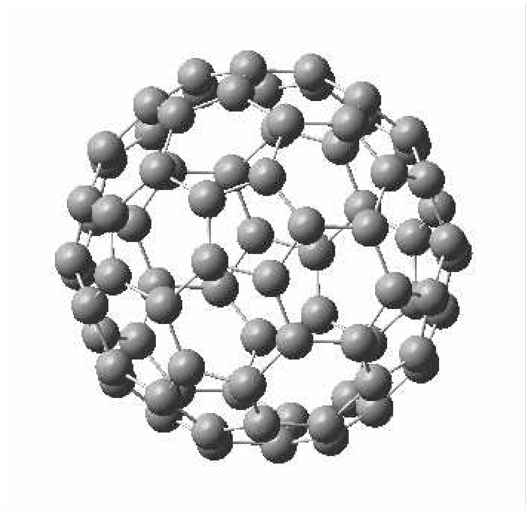
Squashing $H_g(1)$ 227 cm^{-1}



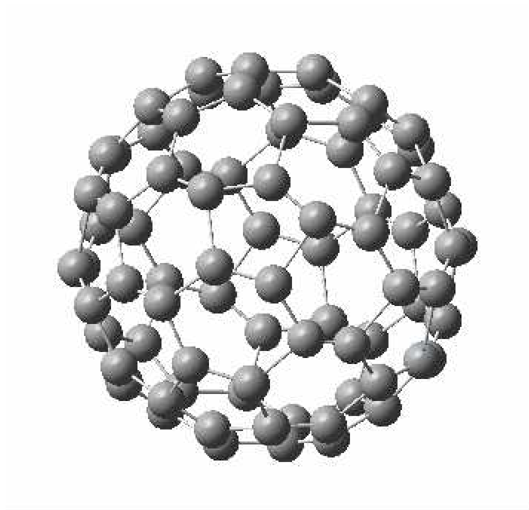
Twist $H_g(2)$ 355 cm^{-1}



Breathing $A_g(1)$ 430 cm^{-1}

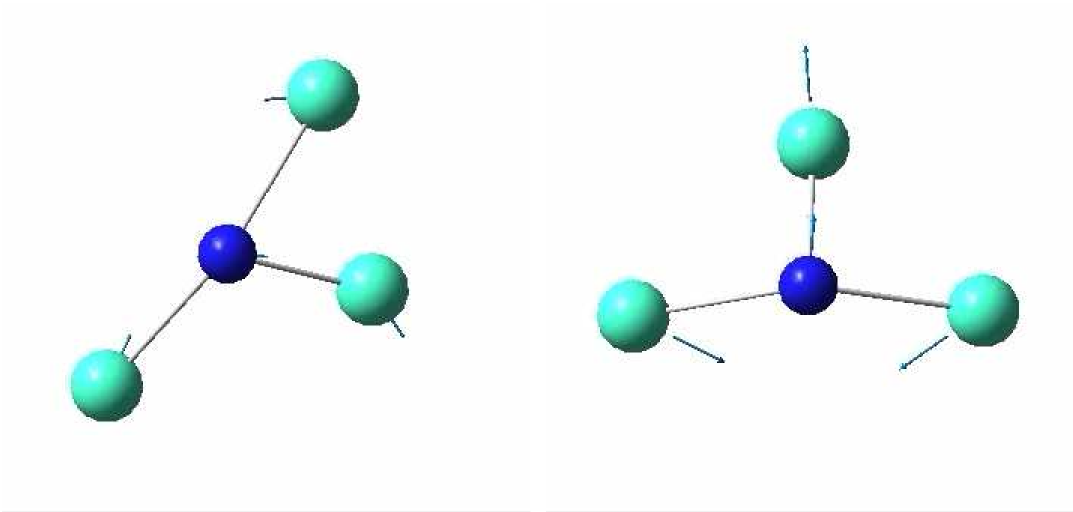


Pentagon Breathing $A_g(2)$ 1471 cm^{-1}

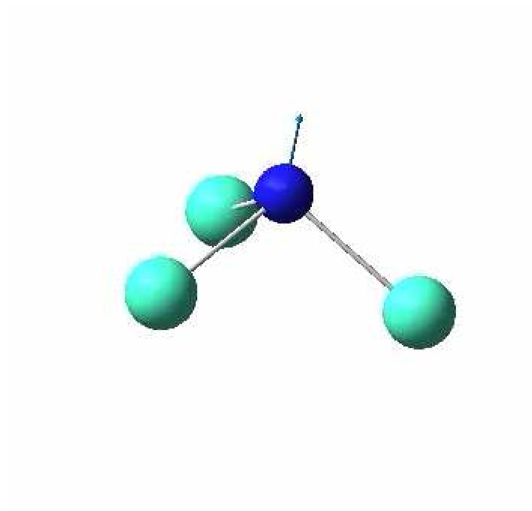


Pentagon Distortion $H_g(8)$ 1517 cm^{-1}

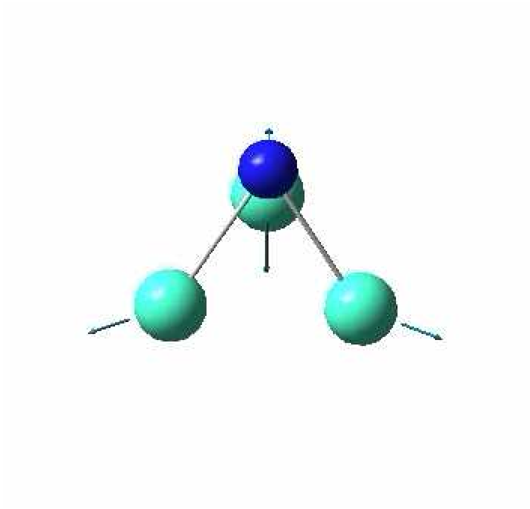
Gd_3N Modes



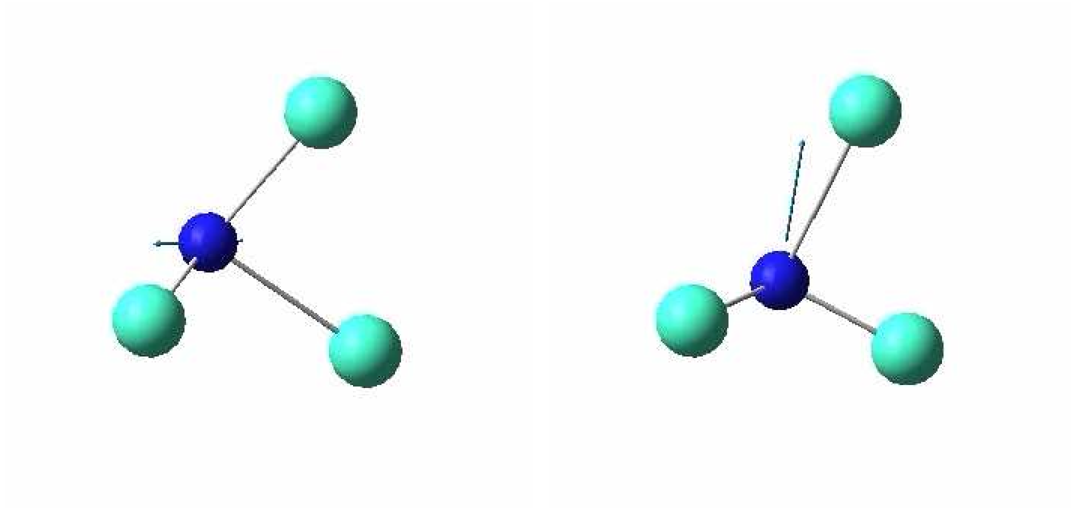
Scissor 94.8 cm^{-1}



Wagging 511.5 cm^{-1}

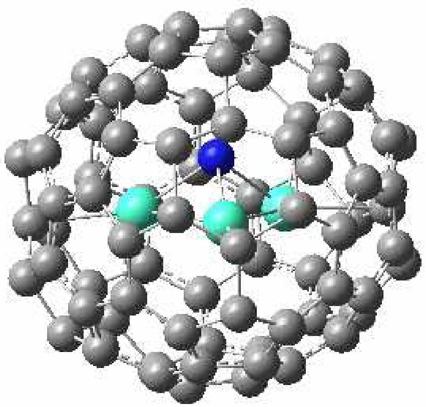


Breathing 112.1 cm^{-1}

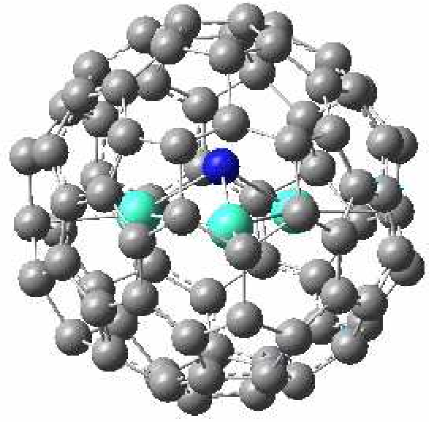


Asymmetric Stretch 747.8 cm^{-1}

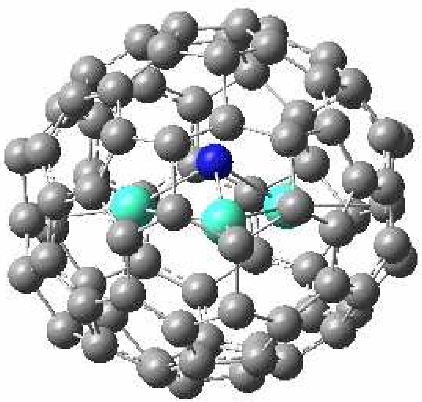
Gd$_3$N@C$_{80}$ Modes



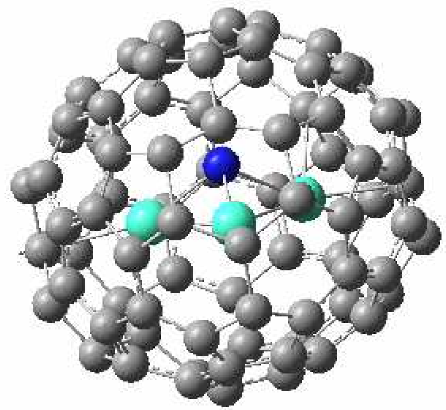
Gd–cage 141.7 cm^{-1} (Exp 165.2 cm^{-1})



H$_g$(1) 217.9 cm^{-1} (Exp 234.5 cm^{-1})



H$_g$(2) 370.7 cm^{-1} (Exp 361.3 cm^{-1})

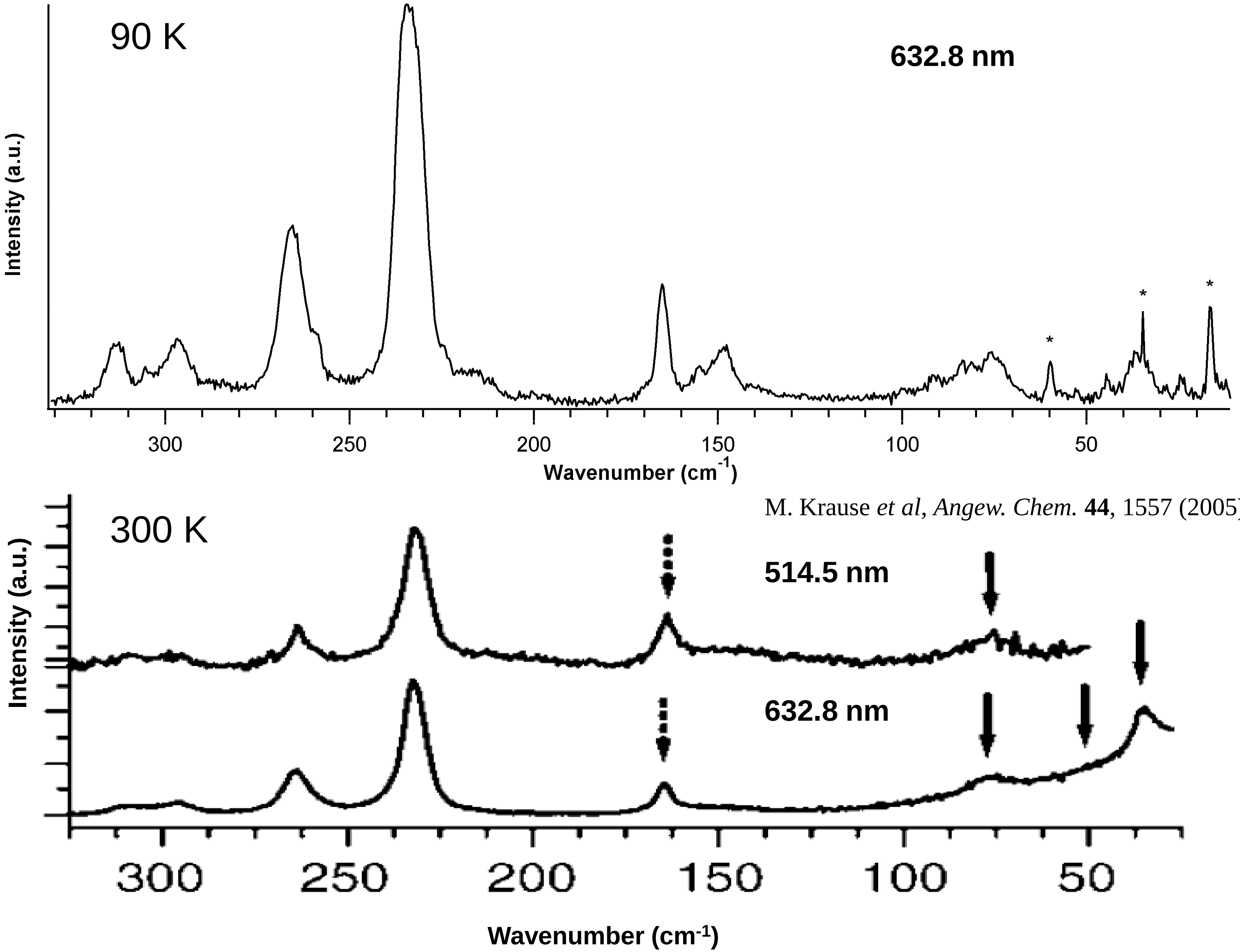


A$_g$(1) 428.5 cm^{-1} (Exp 430.4 cm^{-1})

Raman Spectra of $Gd_3N@C_{80}$ (CNMS)

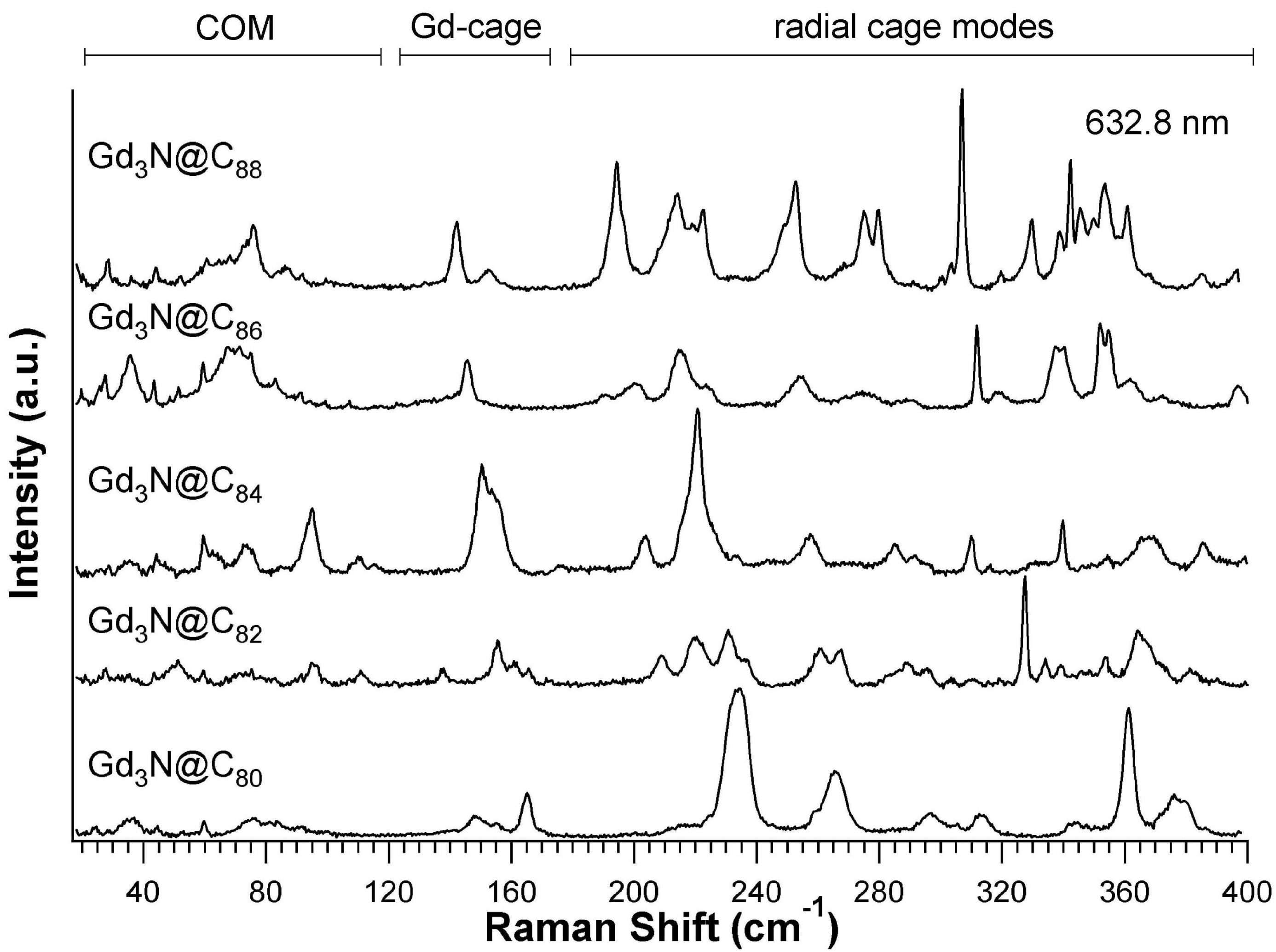
$Gd_3N@C_{80}$ (cm^{-1})
165.2
155
148.4
141.4
100
91.5
83.6
81.2
76
57
52.6
44.6
36.4
35
28.2
24.6

$Gd_3N@C_{80}$ (cm^{-1})
165
77
54
34



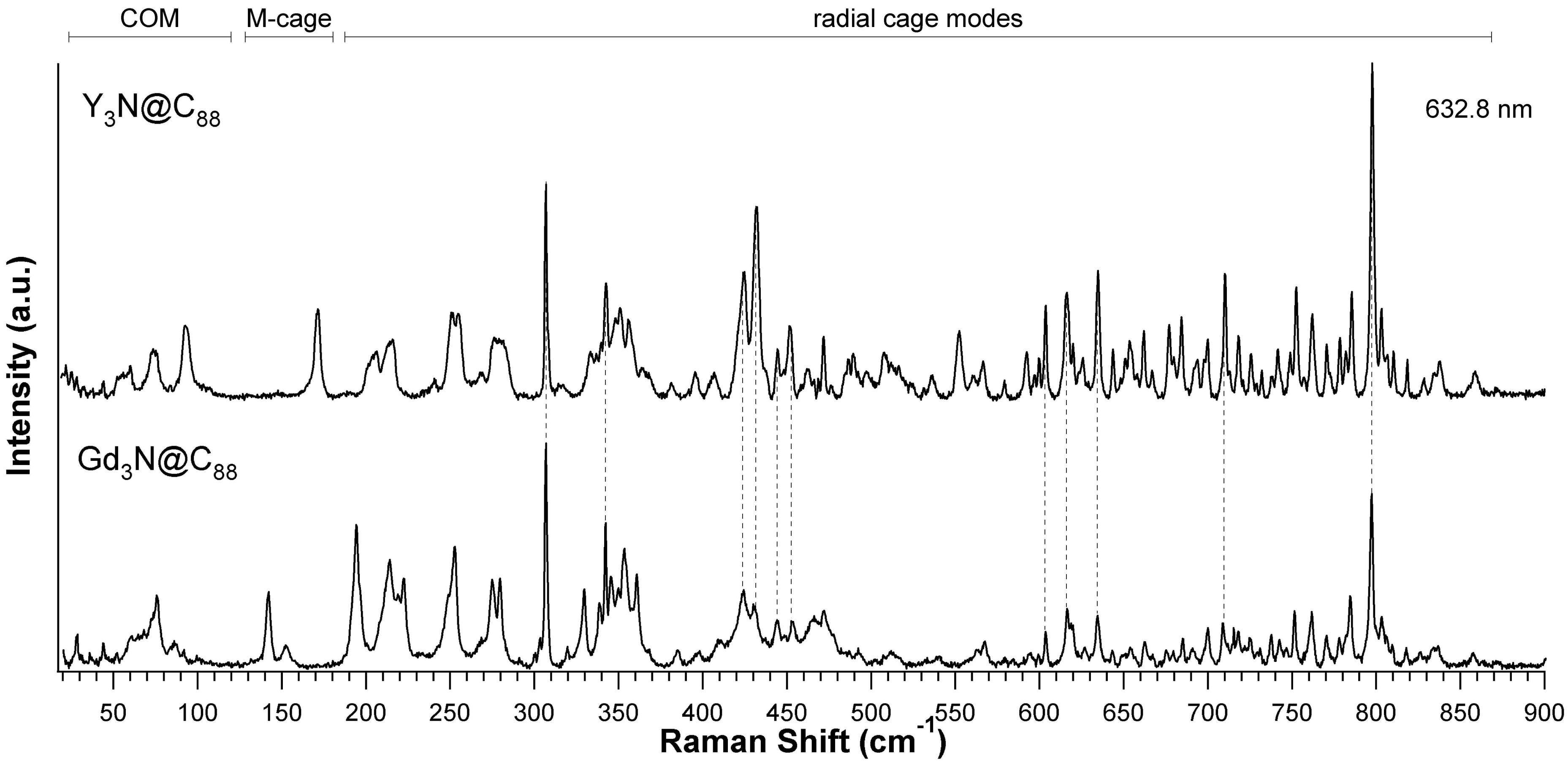
M. Krause *et al*, *Angew. Chem.* **44**, 1557 (2005)

Low-Frequency Raman Spectra of $Gd_3N@C_{2n}$ (90 K)



Analysis of low-energy Raman lines of $Gd_3N@C_{2n}$ (40 ≤ n ≤ 44) taken at 90 K indicating a hindered rotation due to the coupling of the core complex to the cage.

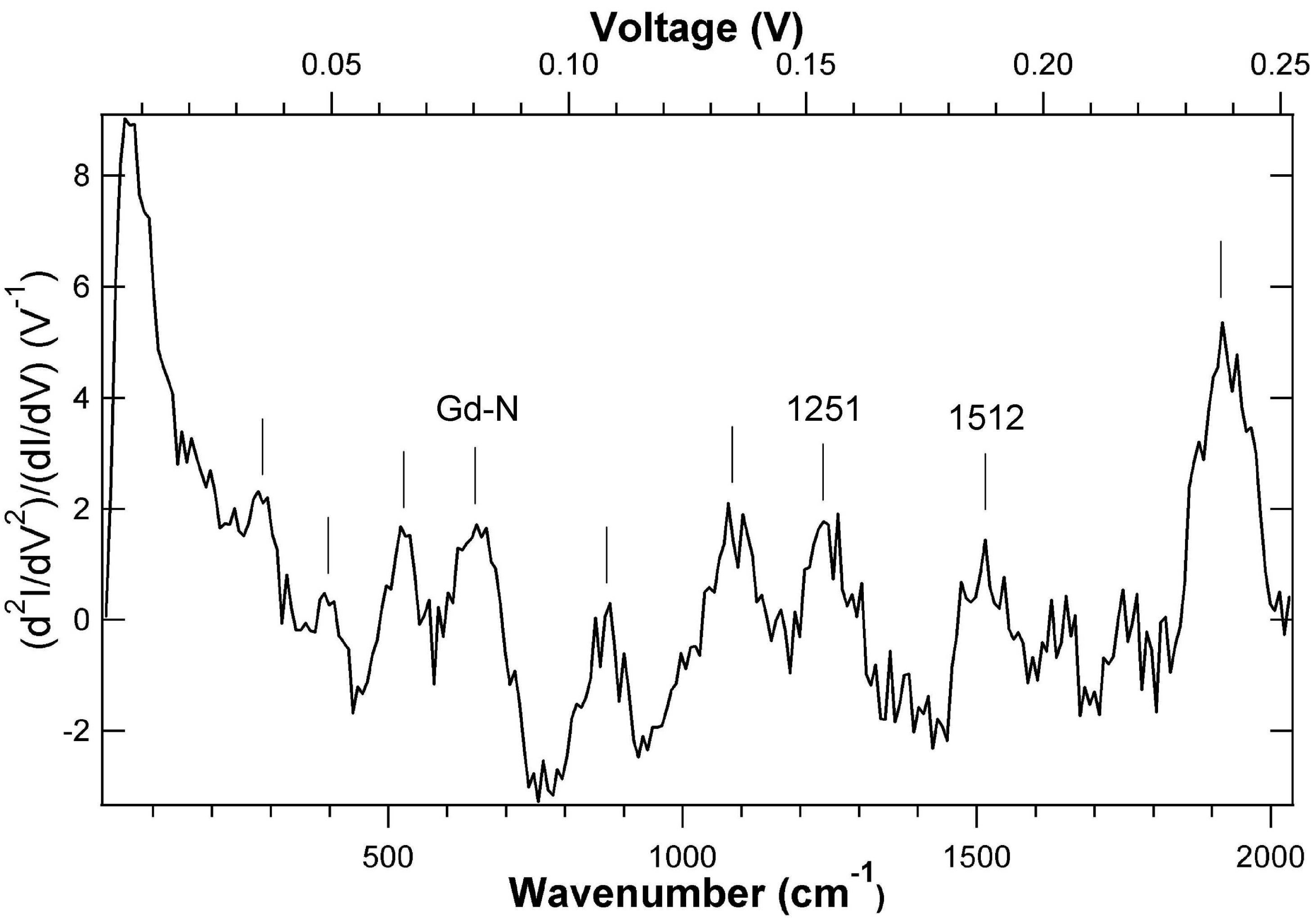
Mode Comparison: $Y_3/Gd_3N@C_{80}$ (90 K)



Comparison of $Y_3N@C_{88}$ and $Gd_3N@C_{88}$ Raman data taken at 90 K. Analysis of the data identifies C_{88} cage modes, hindered rotation modes and center of mass modes. Prominent peak correlations are denoted by dashed lines.

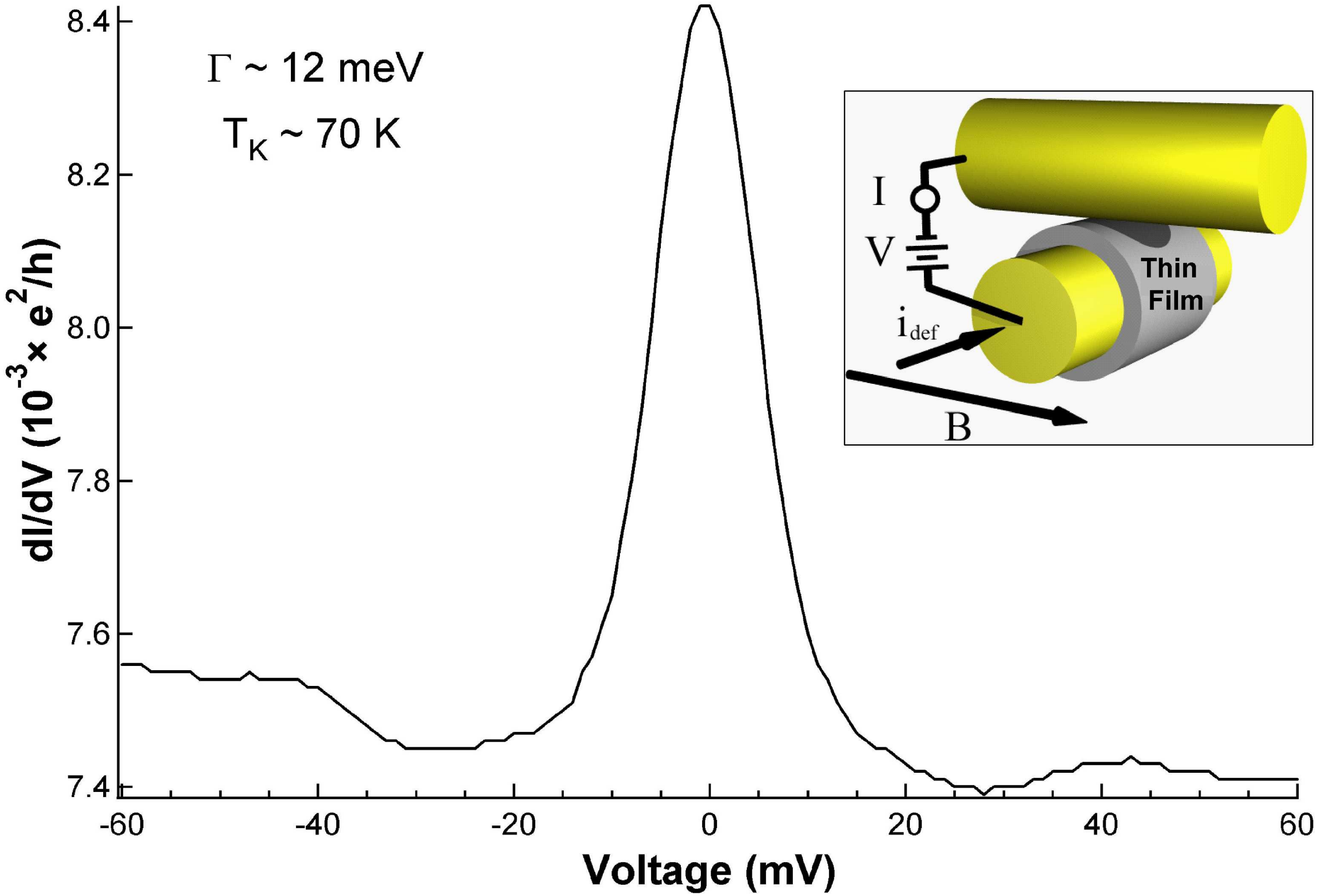
IETS of $Gd_3N@C_{80}$ (90 K)

IETS: no symmetry selection rules

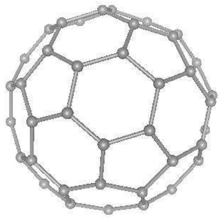


Experimental IETS spectrum obtained for $Gd_3N@C_{80}$ with modulation amplitude V_ω = 4 mV, scan rate = 1.5 mV/s and time constant = 1 s. The anti-symmetric Gd–N stretch mode is identified at 81.6 mV (658 cm^{-1}) as well as Raman C_{80} cage modes at 155.1 mV (1251 cm^{-1}) and 187.5 mV (1512 cm^{-1}).

Kondo Scattering in $Gd_3N@C_{80}$?



Experimental conductance data of Kondo effect and zero-bias anomaly in $Gd_3N@C_{80}$ taken at 4.2 K. Inset shows the experimental setup: Au crossed-wire apparatus forms a junction with the $Gd_3N@C_{80}$ thin film.



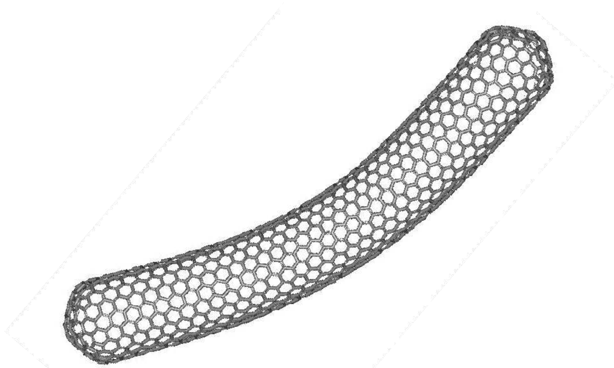
Carbon Nanomaterials Research at UVa

I. Core Capabilities

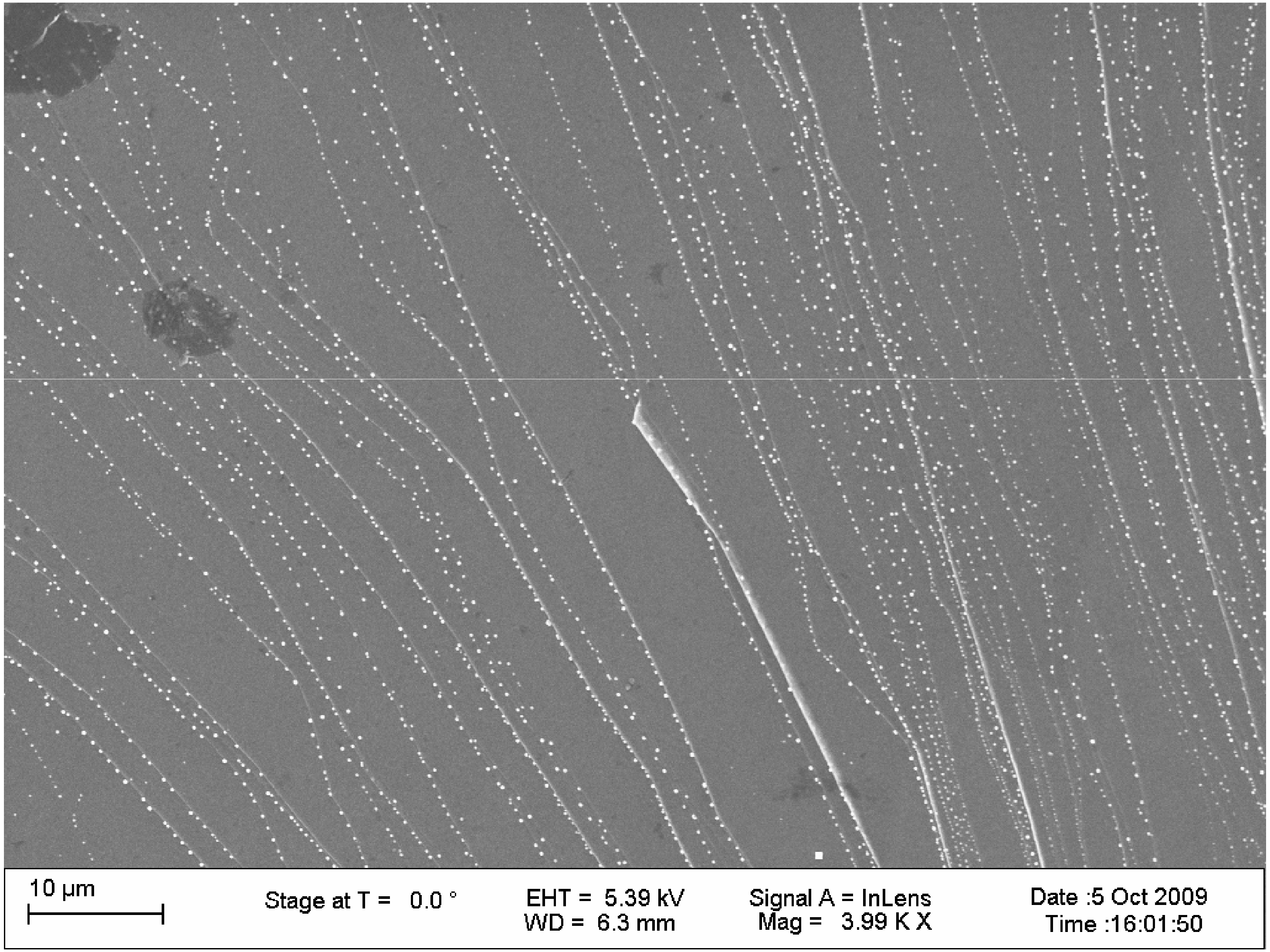
II. Nanotubes

III. Endohedral magnetofullerenes

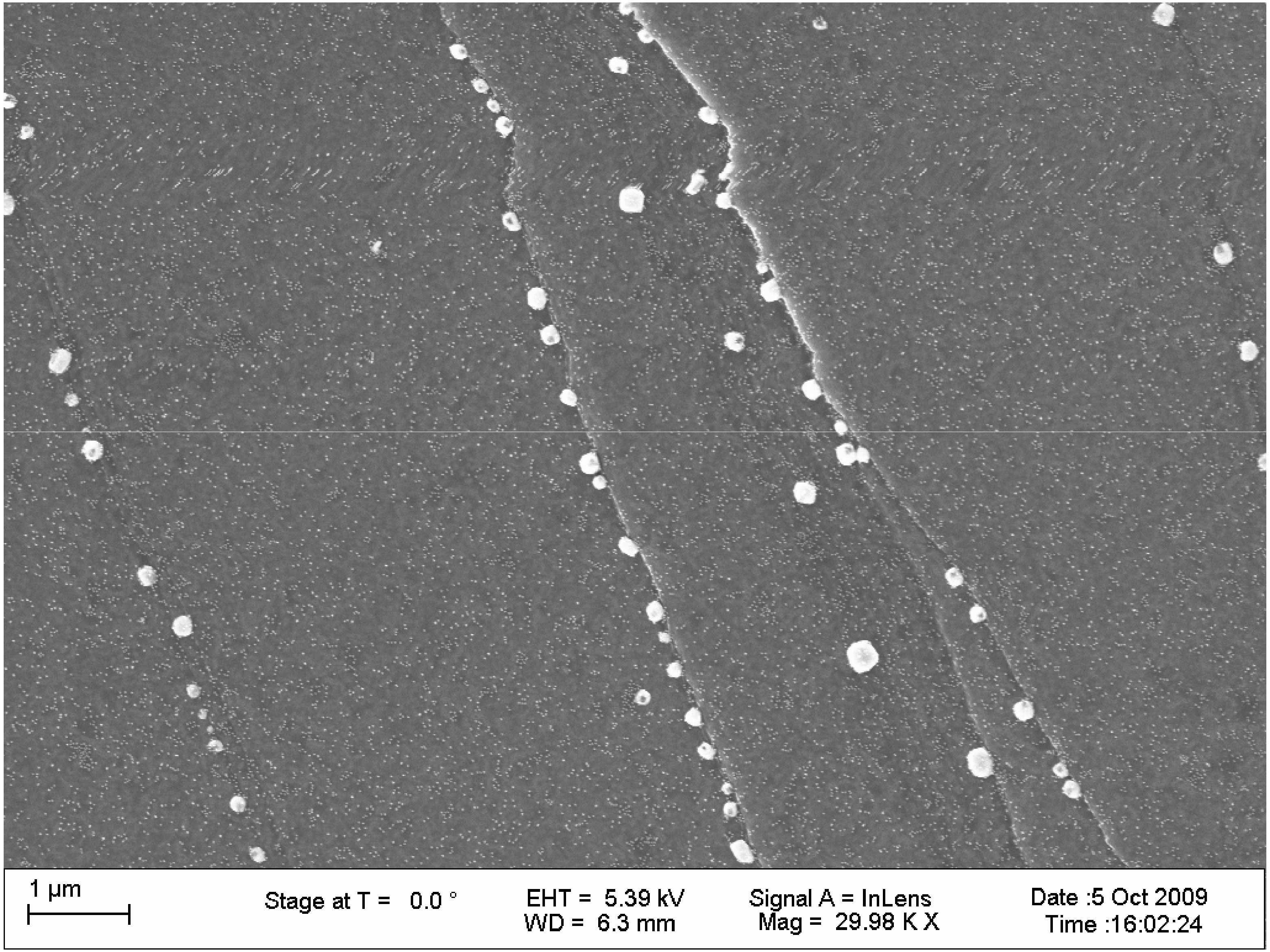
IV. Future Directions



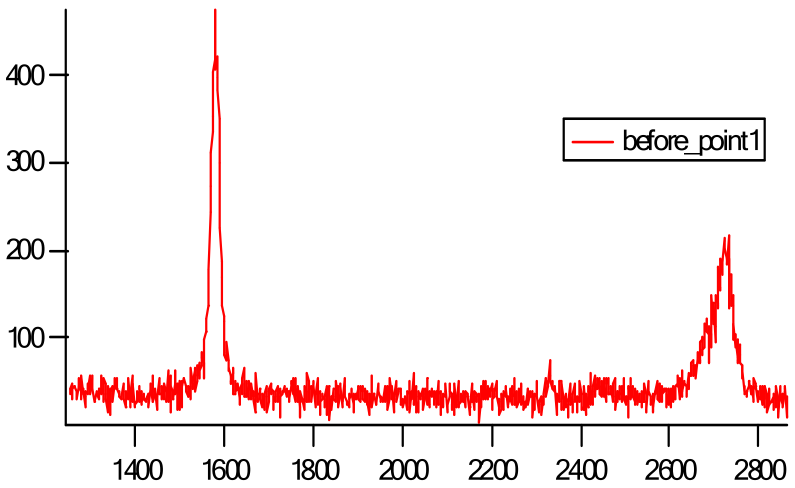
Graphite edge decoration with cationic nanoparticles…

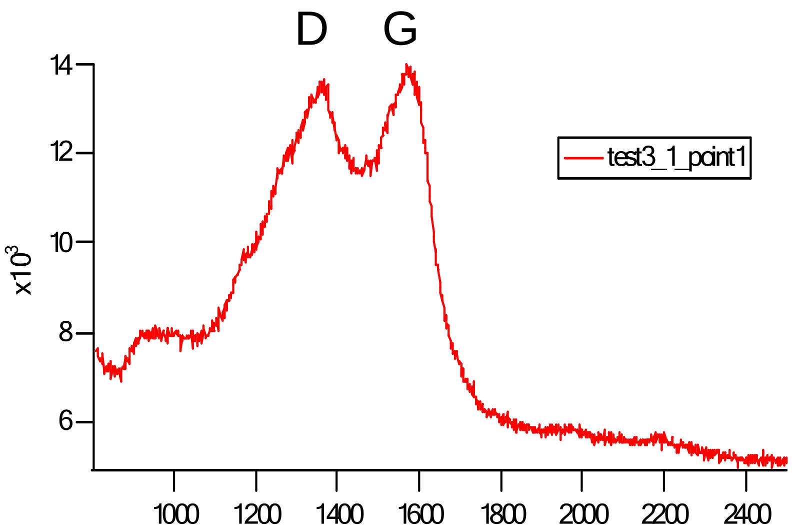


Graphite edge decoration with nanoparticles…



Nanoparticle enhanced Raman Spectrum…



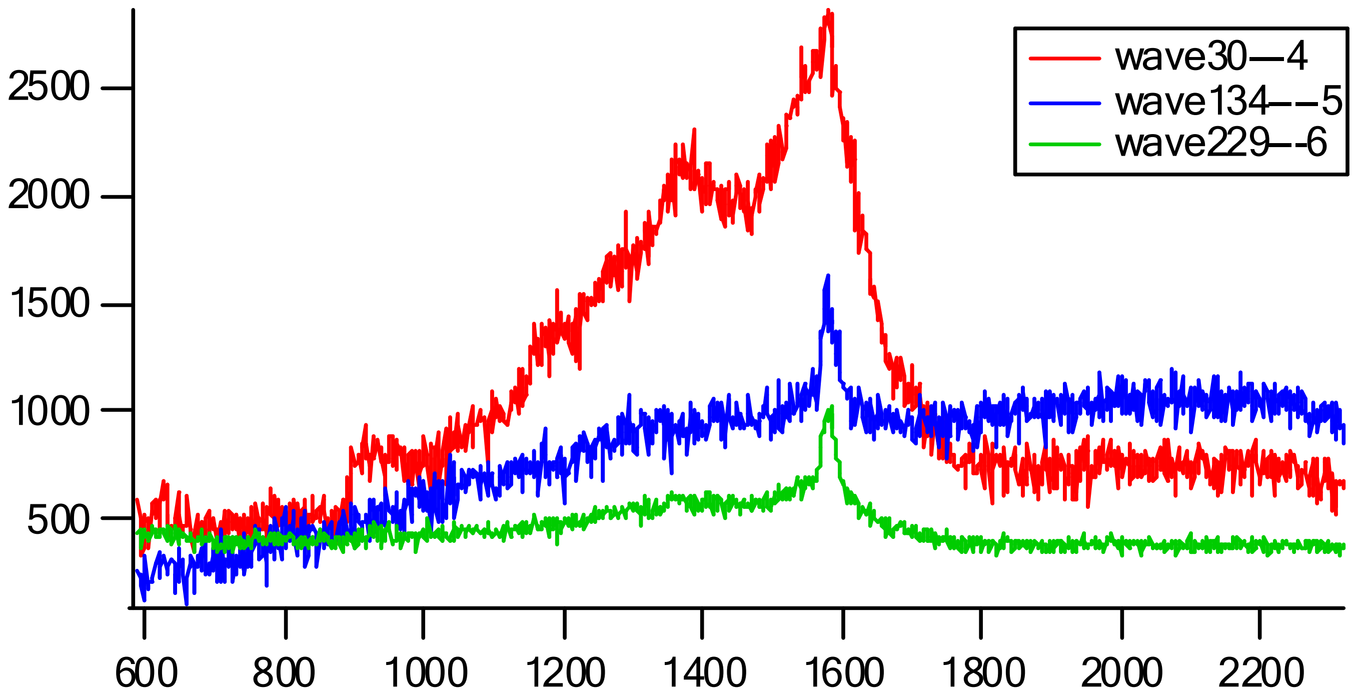


Normal Raman spectrum of HOPG

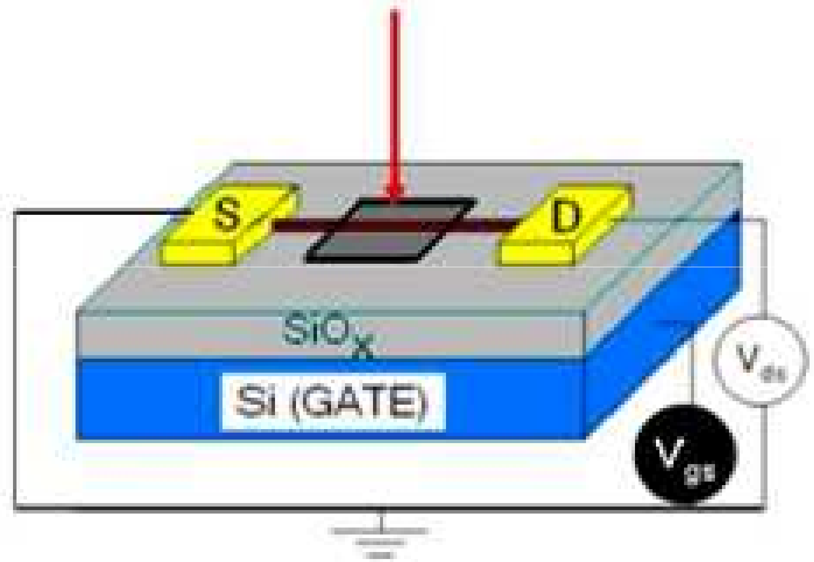
Raman spectrum of HOPG with Ag

(514.5 nm excitation)

Same samples- different points…

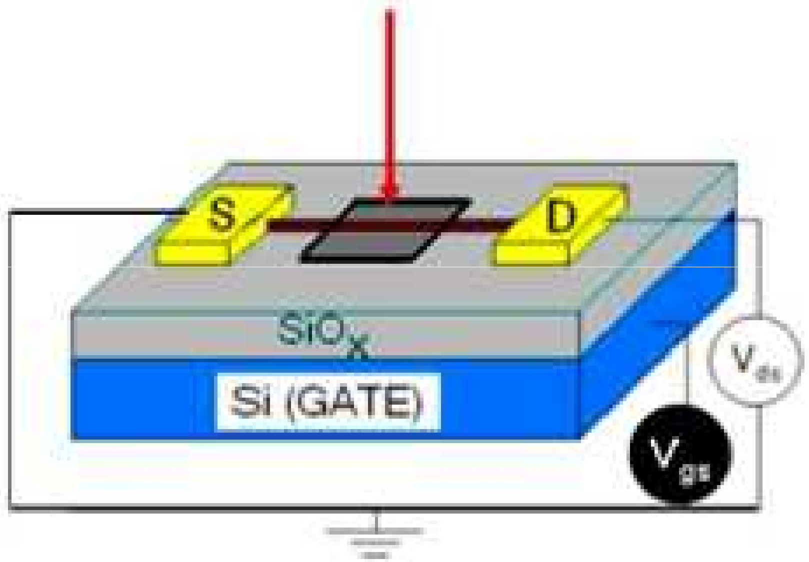


E-beam writing on epi-graphene + transport…



… I/V and Hall measurements in preparation; collab with Lloyd Harriott's group.

E-beam writing on epi-graphene + transport…



… I/V and Hall measurements in preparation; collab with Lloyd Harriott's group.

N.b. Seminar next Thursday by Brian Leroy…

Thursday, October 29, 2009

4:00 PM, Room 204

Physics Building

Brian Leroy

Univ. of Arizona

"Local electronic properties of graphene"

ABSTRACT:

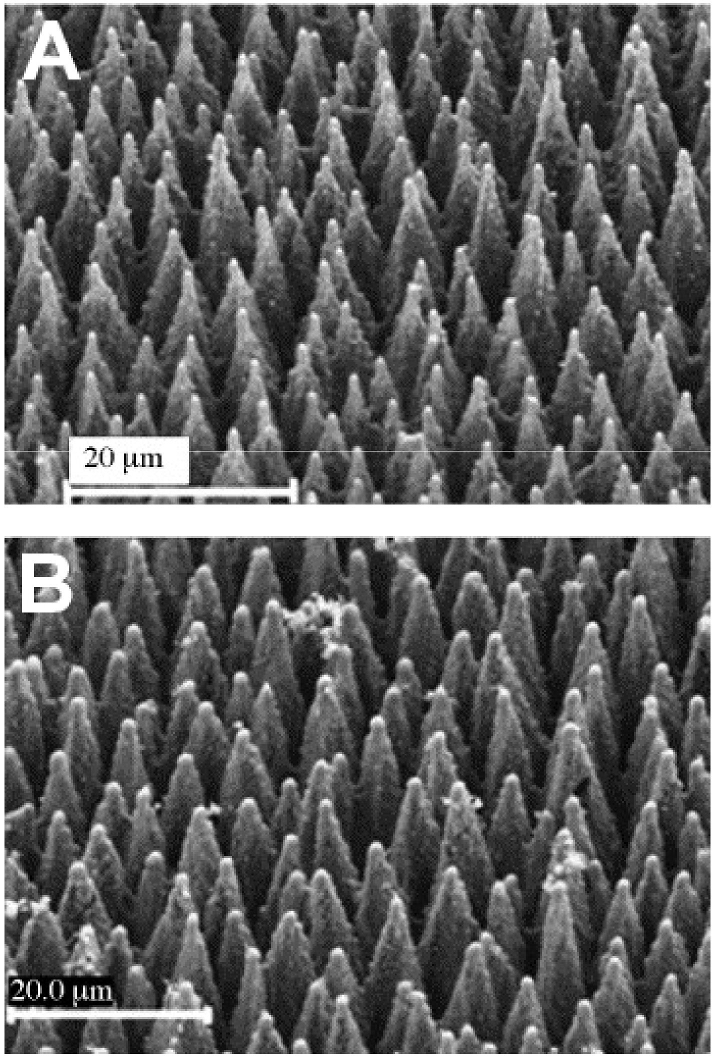
Combining scanning probe microscopy with electrical transport measurements is a powerful approach to probe low-dimensional systems. The local information provided by scanning probe microscopy is invaluable for studying effects such as electron-electron interactions and scattering. Using this approach, **we have probed the local electronic properties of mono- and bilayer graphene with atomic resolution. We studied the effect of ripples, charged impurities and defects on the local density of states.** We find that long-range scattering from ripples and impurities shifts the Dirac point leading to electron and hole puddles. Short-range scattering from lattice defects mixes the two sublattices of graphene and tends to be strongly suppressed away from the Fermi energy. In addition, **in bilayer graphene we observe an opening of a band gap due to the application of a transverse electric field.**

Artificial Cilia for the Investigation of Cell Cooperativity in Wound Healing*

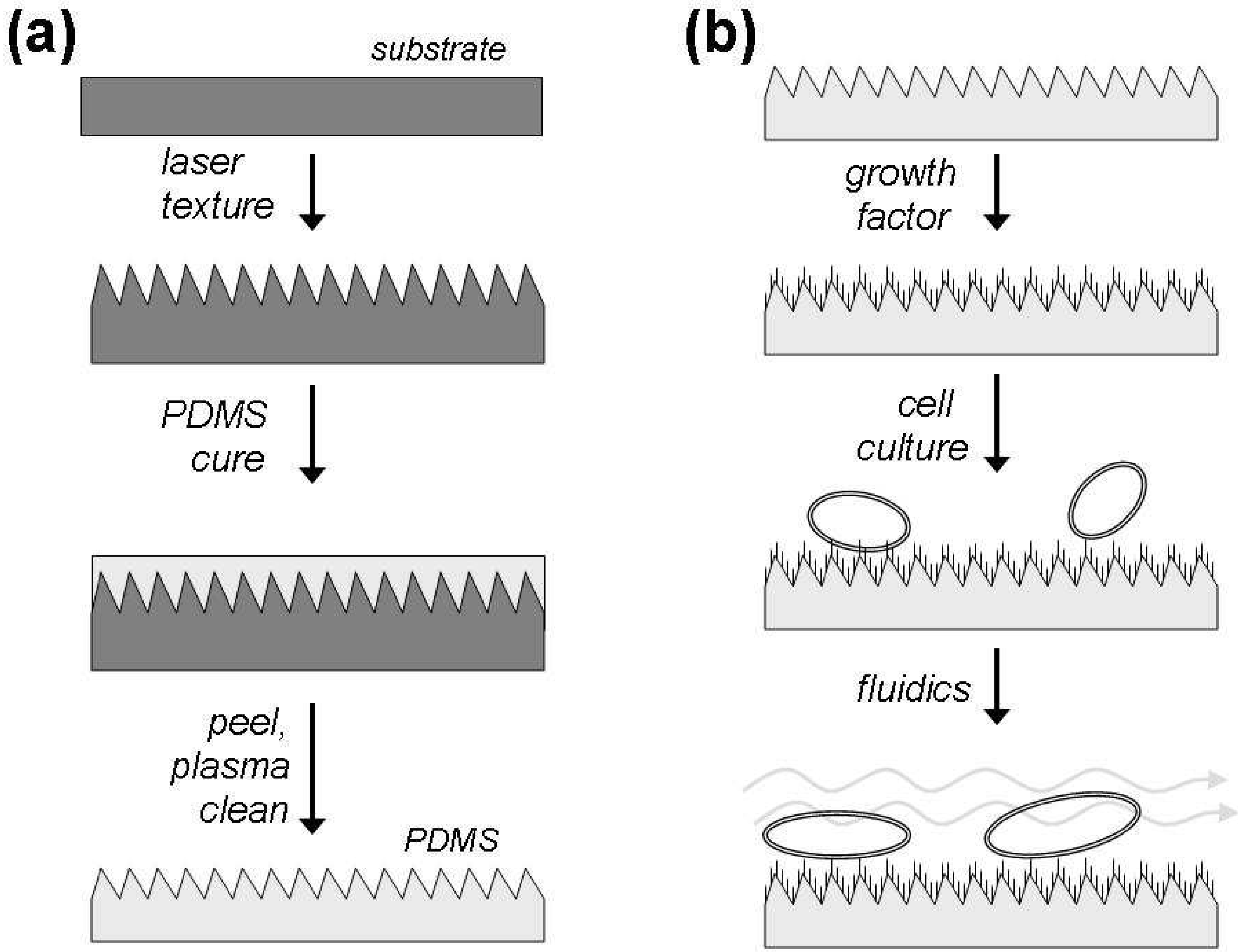
Keith Williams	Physics
Brian Helmke	Biomedical Engineering
Mool Gupta	Electrical & Computer Engineering
Kurt Kolasinski	Chemistry, West Chester University

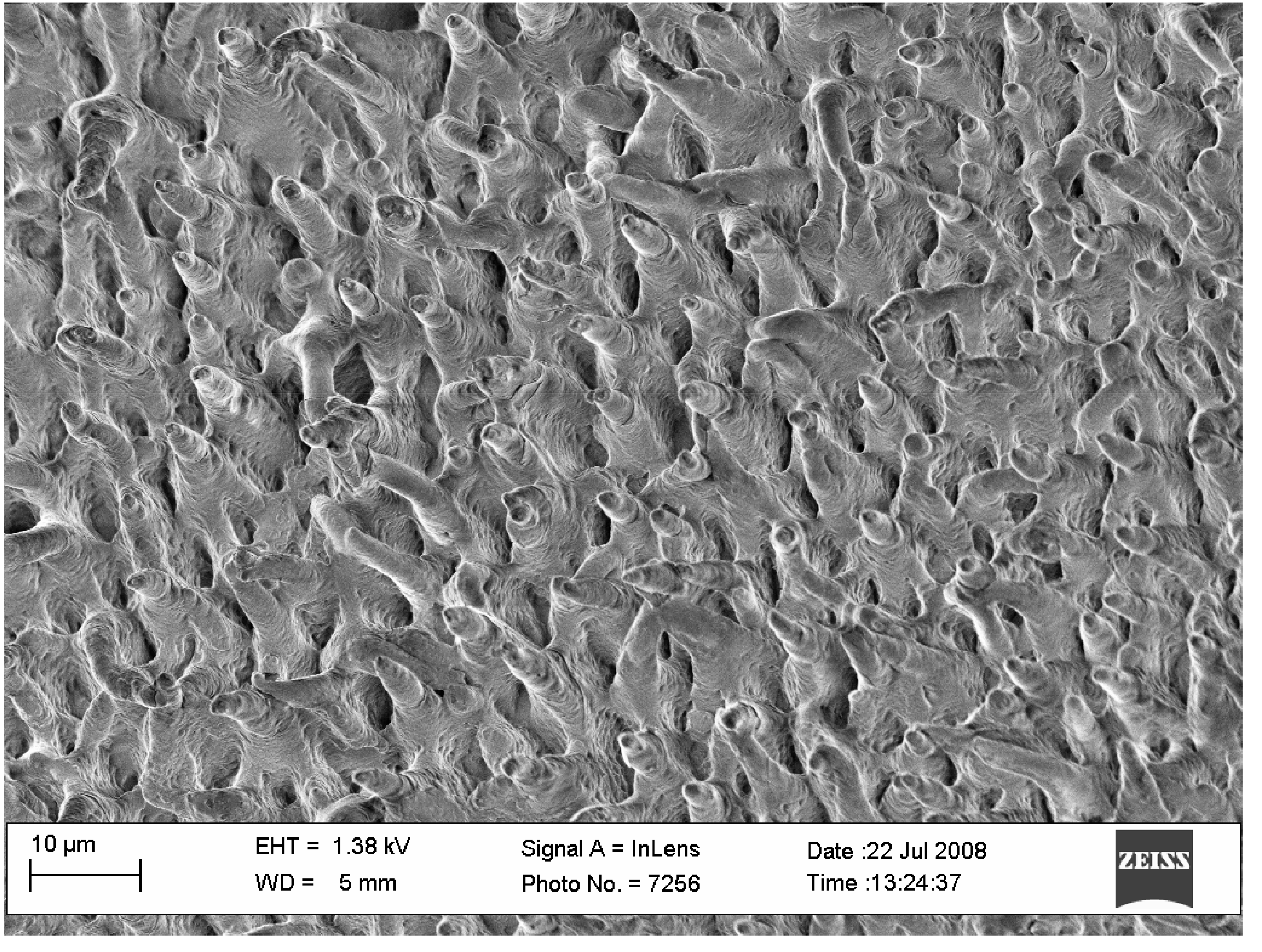
Undergrad currently working on this project: Aagya Mathur

*Work seeded in Fall 2008 by NanoSTAR



Nanopillars fabricated in the group of co-PI Gupta (UVa).


(a)
substrate
laser texture
PDMS cure
peel, plasma clean
PDMS
(b)
growth factor
cell culture
fluidics


10 µm
EHT = 1.38 kV
WD = 5 mm
Signal A = InLens
Photo No. = 7256
Date :22 Jul 2008
Time :13:24:37
ZEISS

Current group:

Drs. Brian Burke (graduating Fall ‘09)
Drs. Jack Chan (graduating Spring ‘10)
Drs. Caixia Bu
Drs. Nattawut (a.k.a. Tom) Anuniwat
Kridsanaphong (a.k.a. Tor) Limtragool
Aagya Mathur

Collaborations:

Avik Ghosh (UVa, ECE, theory)
Lloyd Harriott (UVa, ECE, graphene device fab)
Giovanni Zangari (UVa, graphene electrochem)
Harry Dorn (VT, endofullerenes)
Kurt Gaskill (NRL, epi graphene)
Nathan Guisinger (Argonne, epi-graphene)
James Kushmerick (NIST, IETS on fullerenes)
David Geoghegan (Oak Ridge CNMS, high-res, low freq. Raman)
Luna Corp. Blacksburg and Danville (193nm superlens; magneto-Raman)

Funding: NSF, DARPA, UVa NanoSTAR