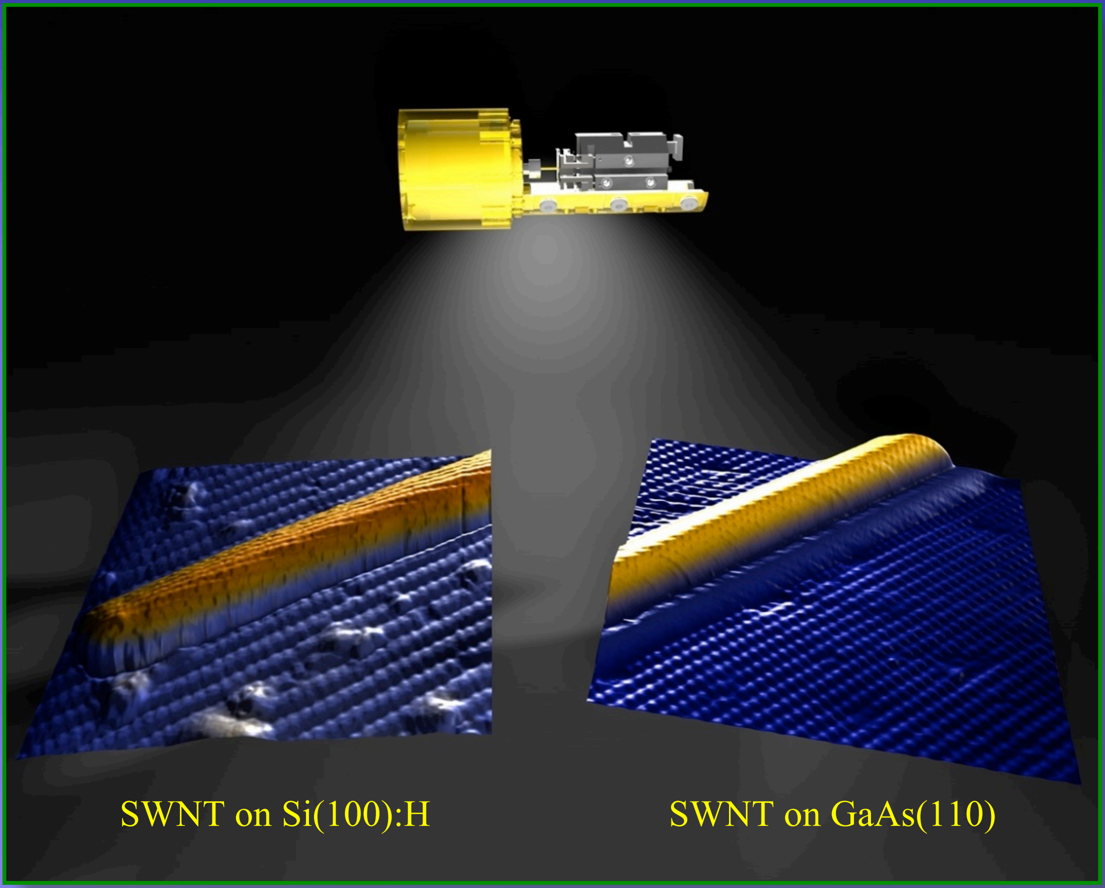
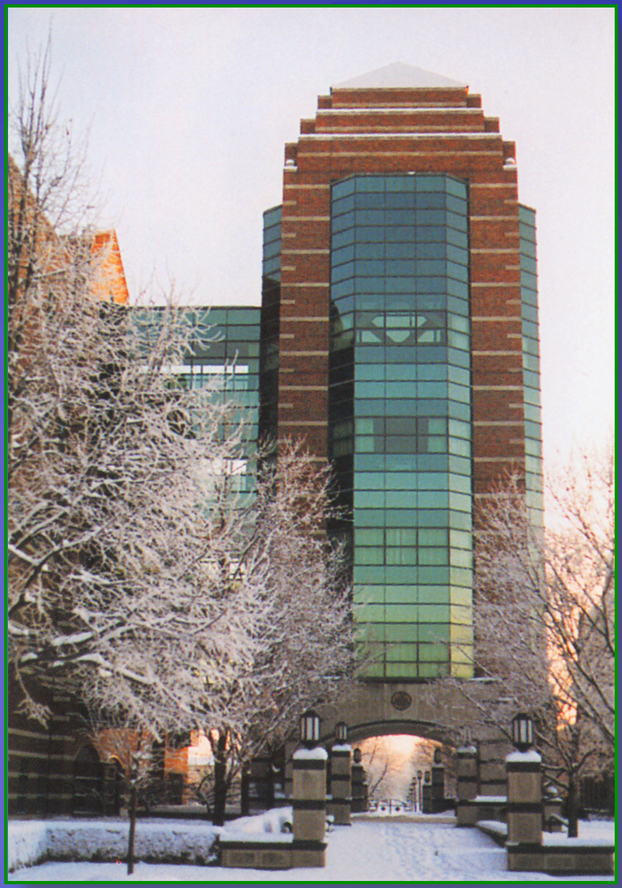
Carbon Nanotechnology: Scientific and Technological Issues

Joseph W. Lyding
Department of Electrical and Computer Engineering and Beckman Institute
University of Illinois at Urbana-Champaign





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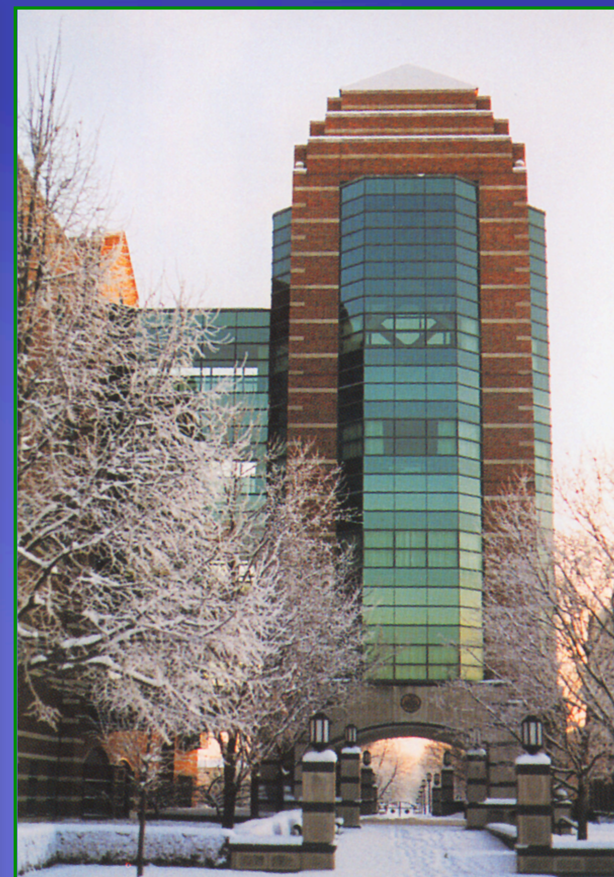
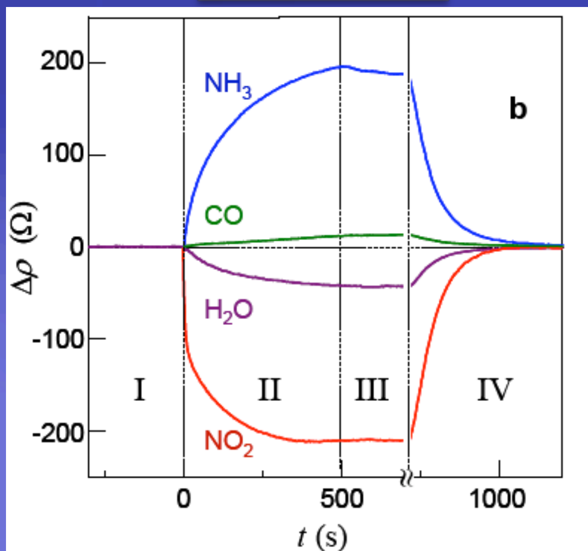
Outline

- Carbon Nanotechnology
- SWNTs on Silicon
- SWNTs III-V Semiconductors
- Graphene
- Ultra-Sharp (r < 1nm) STM Probes



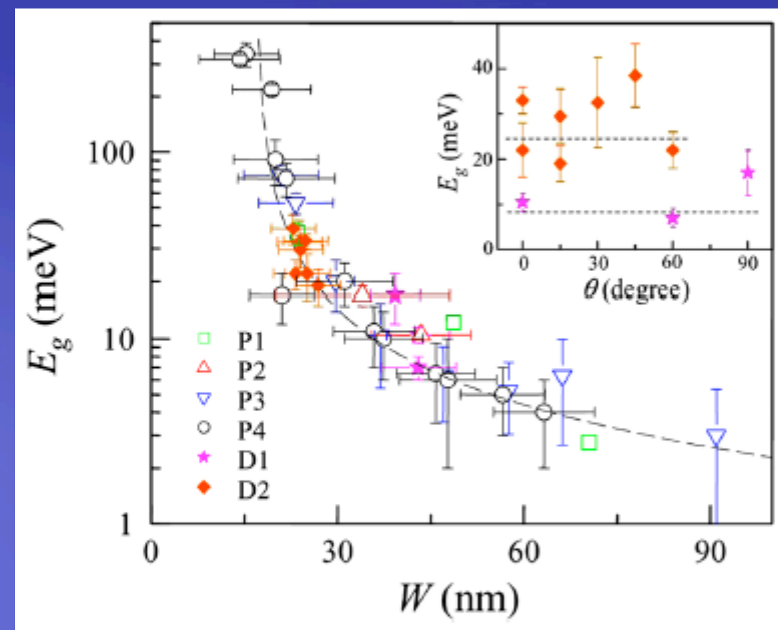
Graphene and Nanotube Nanoelectronics

Sensors



Nature Mat. 6, 652 (2007).

Bandgap engineering



Phys. Rev. Lett. 98, 206805 (2007).

Advantageous properties for nanoelectronics

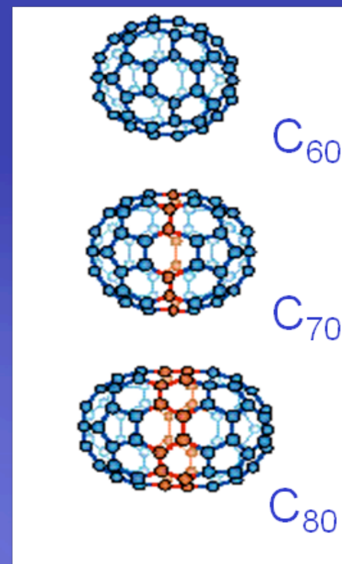
All Surface -> Good for Sensors

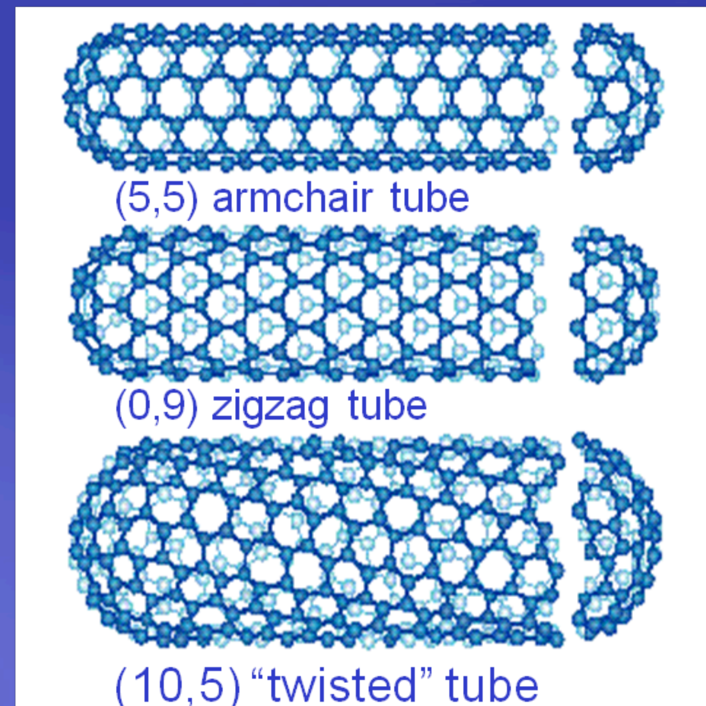
High Mobilities μ = 20,000 $cm^2/V{\cdot}s$ (Si MOSFET – 600 $cm^2/V{\cdot}s$, InSb – 30,000 $cm^2/V{\cdot}s$)

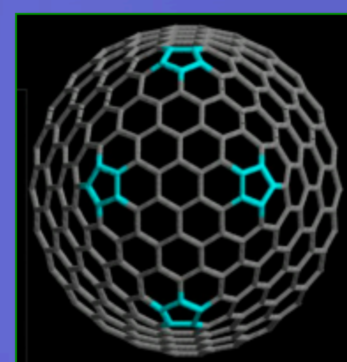
Bandgap Engineering

Carbon Nanotubes

- Fullerenes discovered by Smalley, Kroto, & Curl 1985 (1996 Nobel prize)
- Nanotubes discovered by Iijima in 1991 can be seen in its structure as an extension of a buckyball
- Most nanotubes are bundled together (by van der Waals interactions), forming ropes

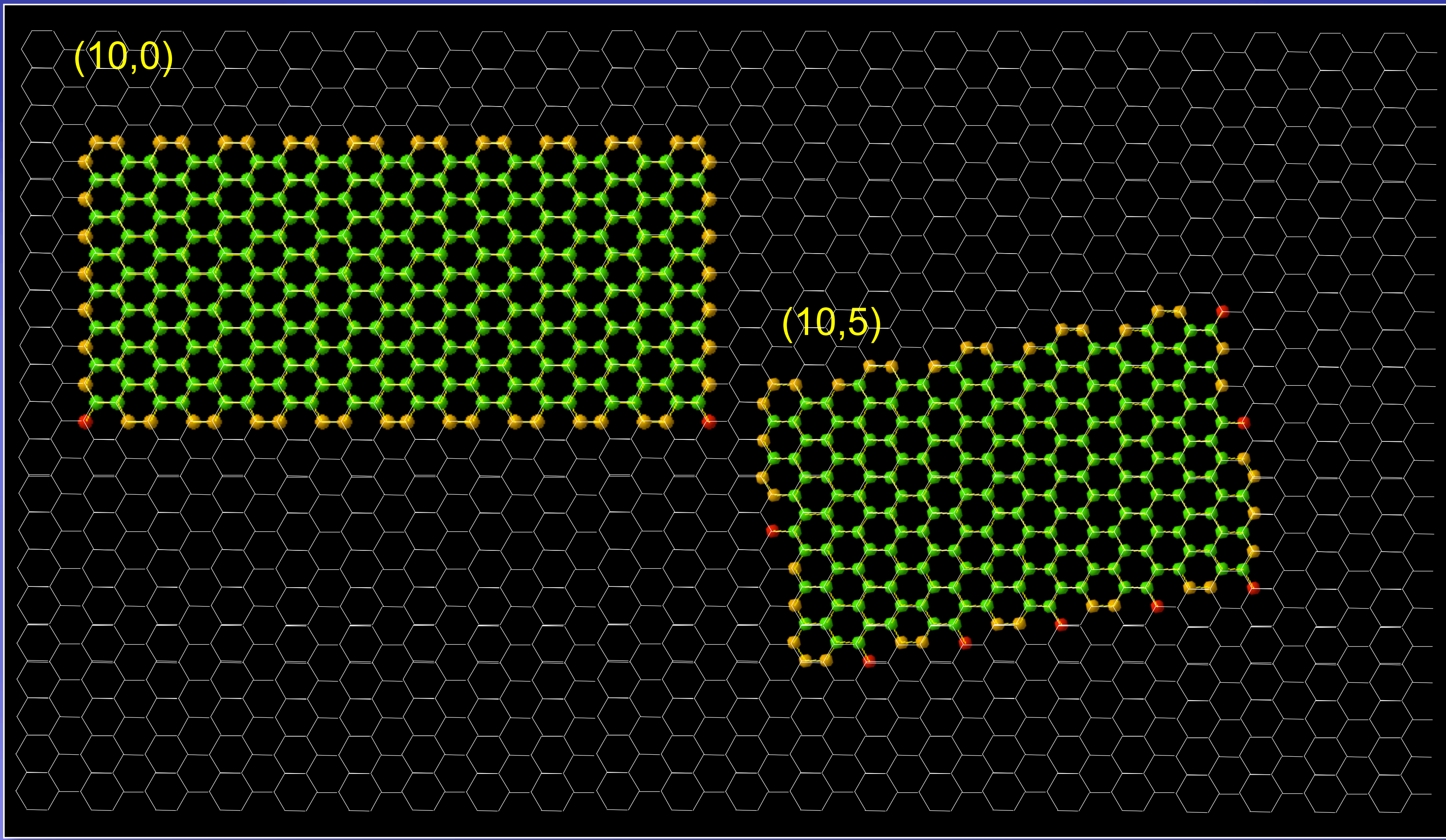




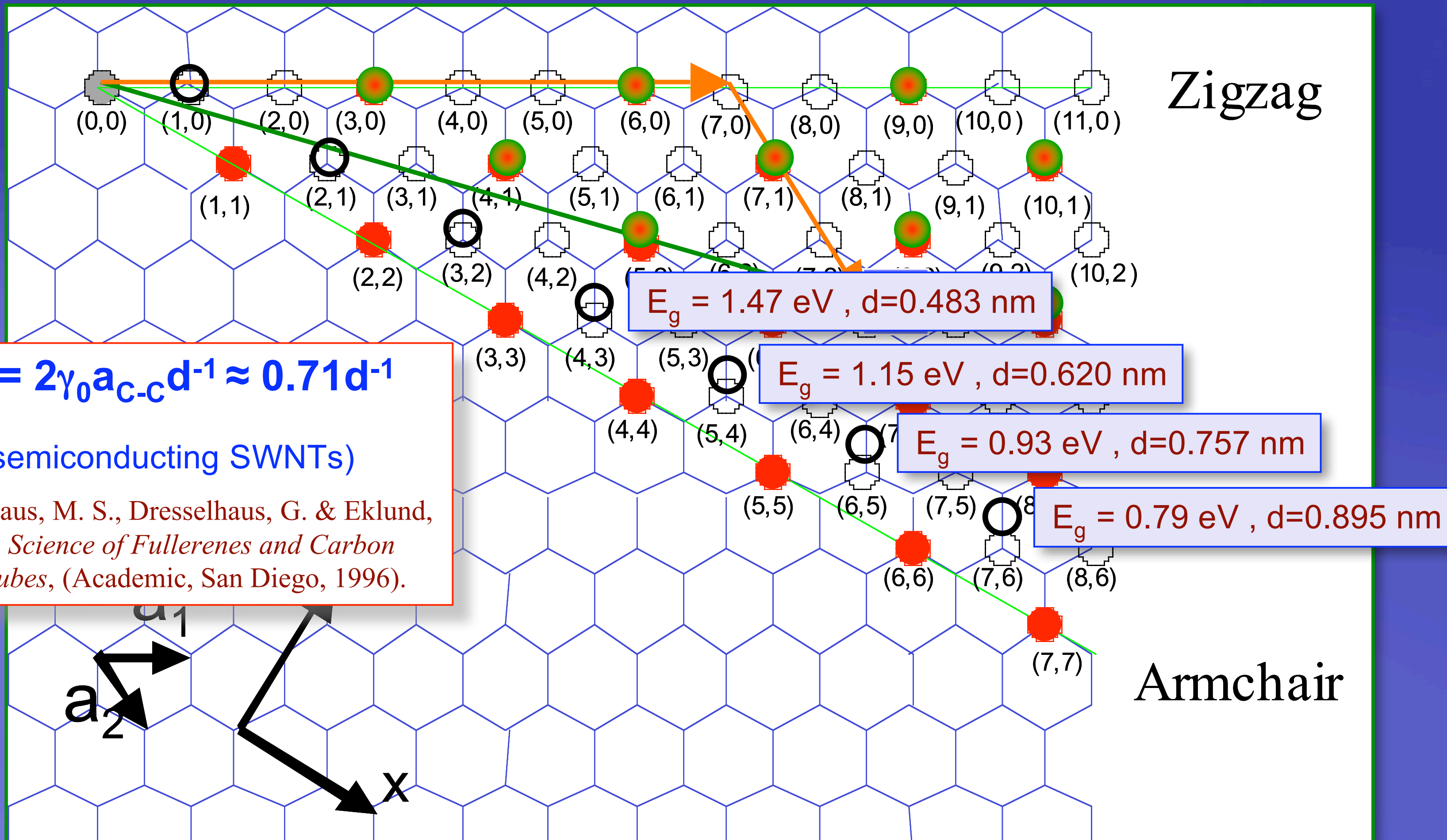


To close the CNT, the cap need pentagons as declination points

Carbon Nanotubes - Structure



Electronic Properties of Carbon Nanotubes



$$E_g = 2\gamma_0 a_{C\text{-}C} d^{-1} \approx 0.71 d^{-1}$$

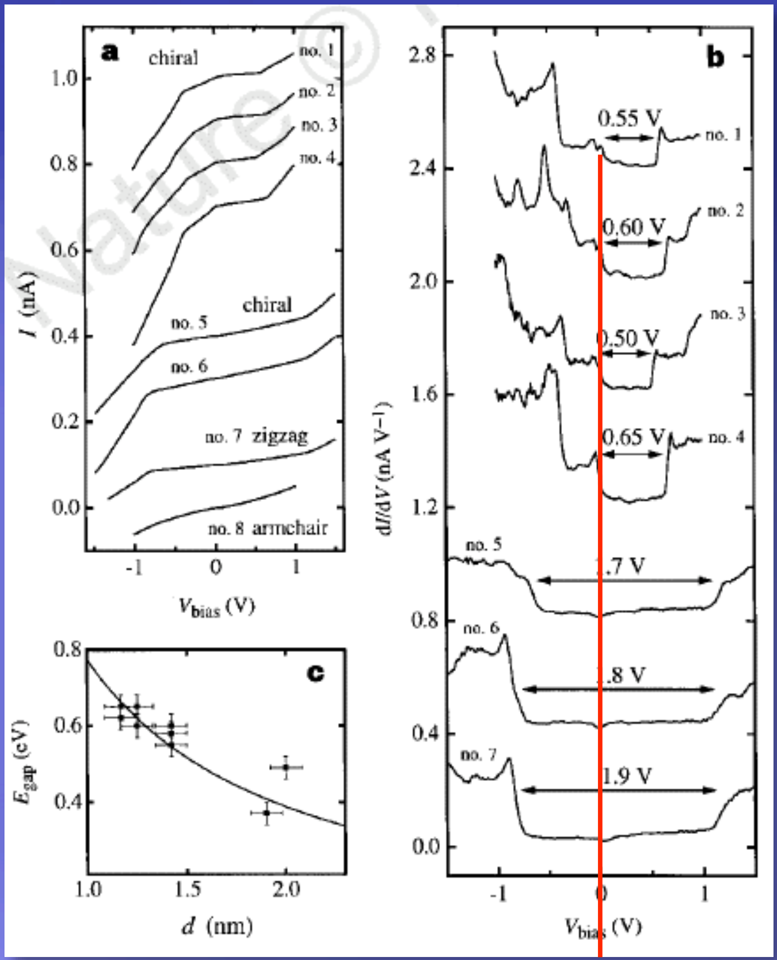
(semiconducting SWNTs)

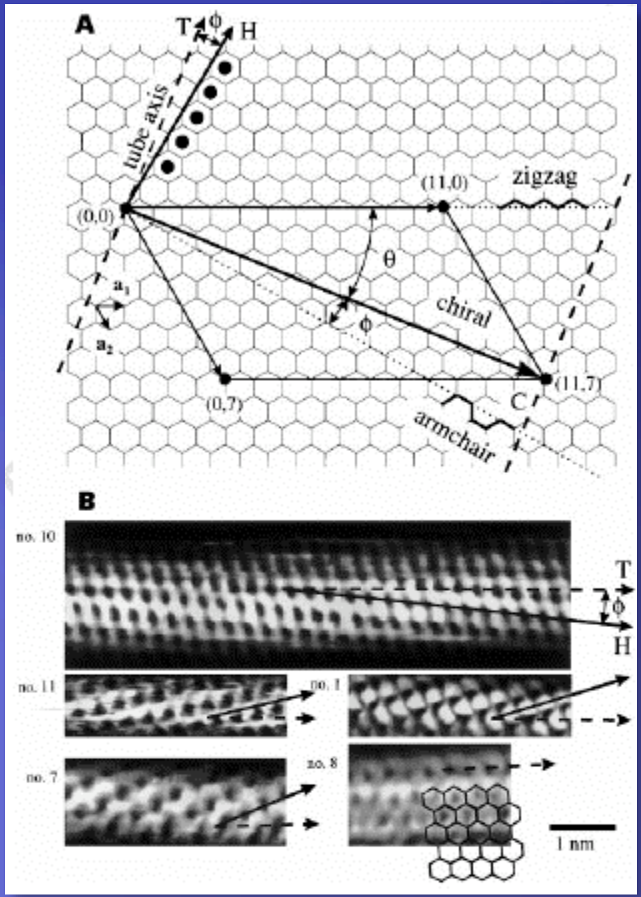
Dresselhaus, M. S., Dresselhaus, G. & Eklund, P. C., *Science of Fullerenes and Carbon Nanotubes*, (Academic, San Diego, 1996).

$$C = na_1 + ma_2$$

- (n,n) → Metallic
- n-m = 3j → Metallic
- All Other → Semiconducting

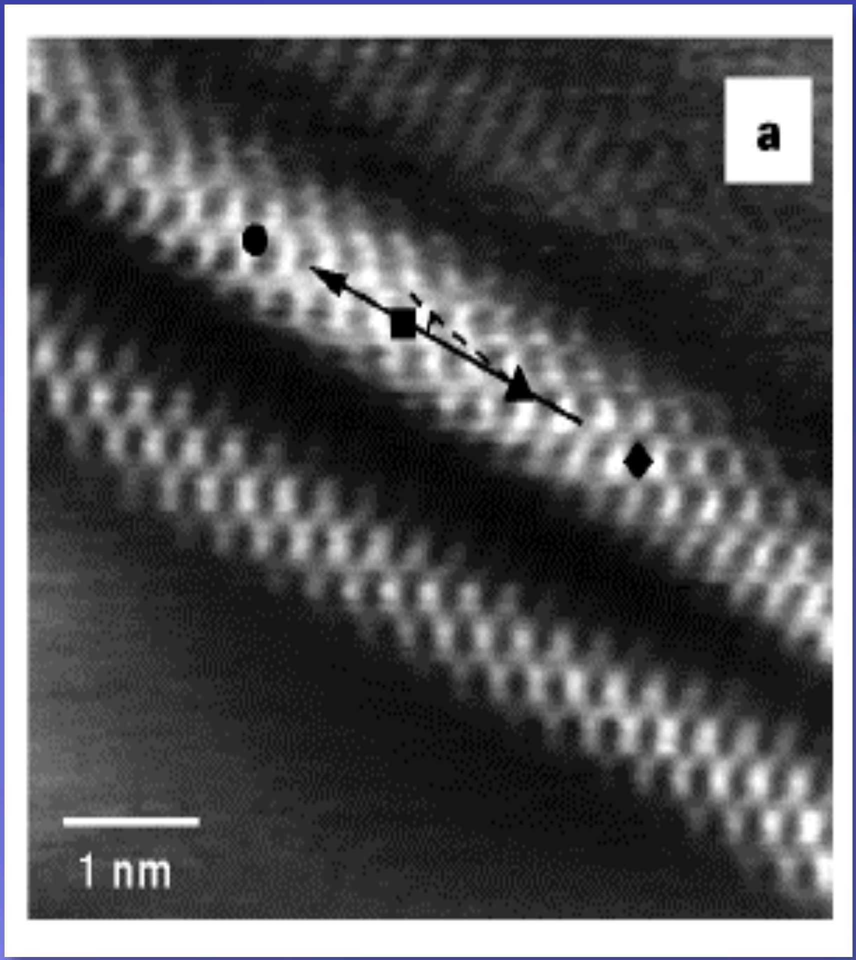
STM/STS of SWNTs

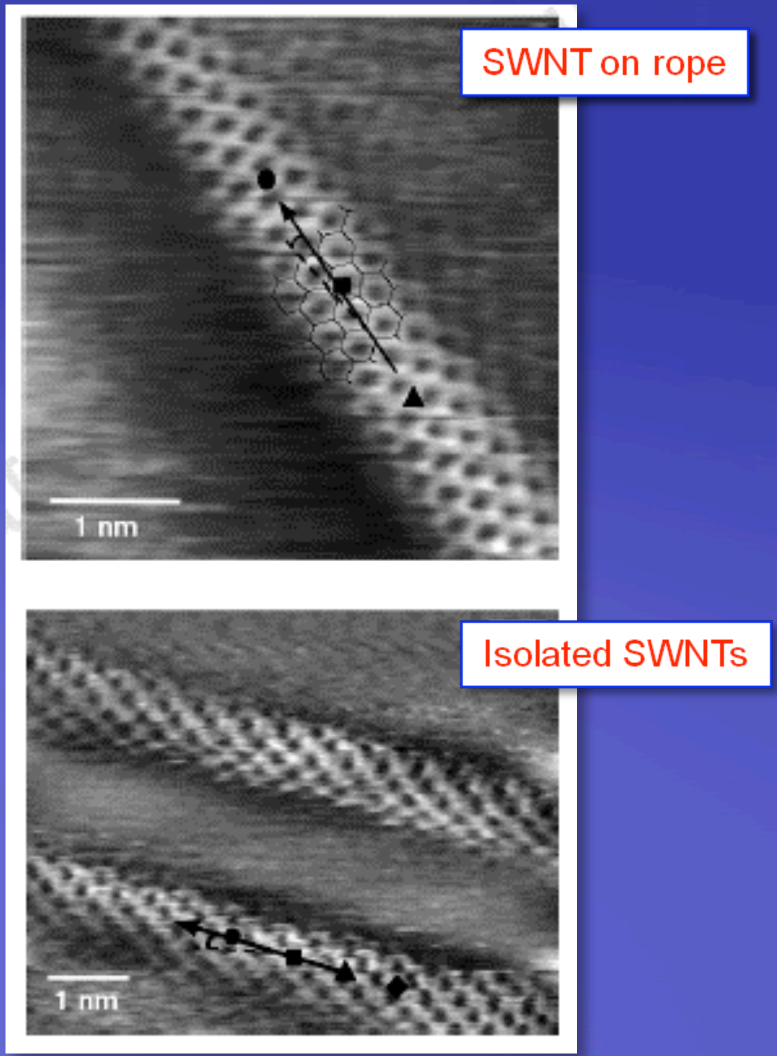




Jeroen W. G. Wildoer, Liesbeth C. Venema, Andrew G. Rinzler, Richard E. Smalley & Cees Dekker, Nature 391, 59 (1998).

STM of SWNTs

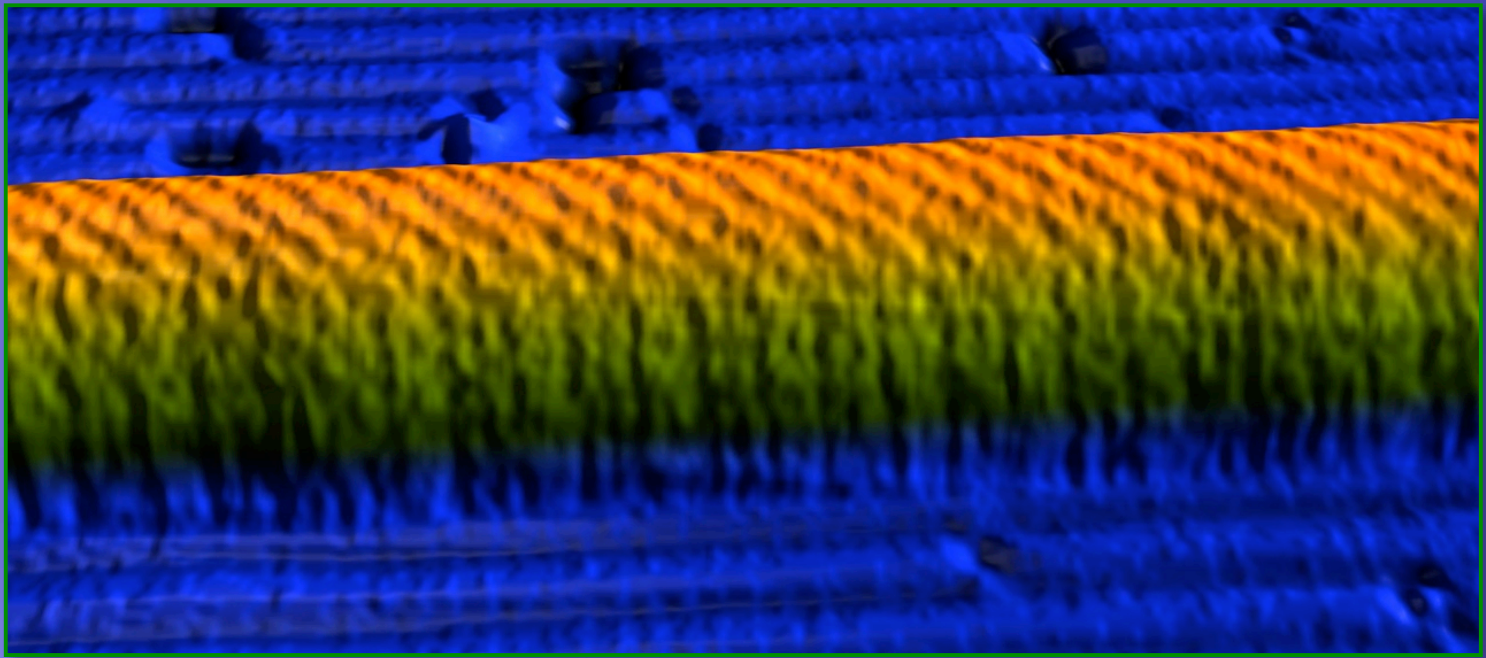




Teri Wang Odom*, Jin-Lin Huang*, Philip Kim, Charles M. Lieber, Nature 391, 62 (1998)

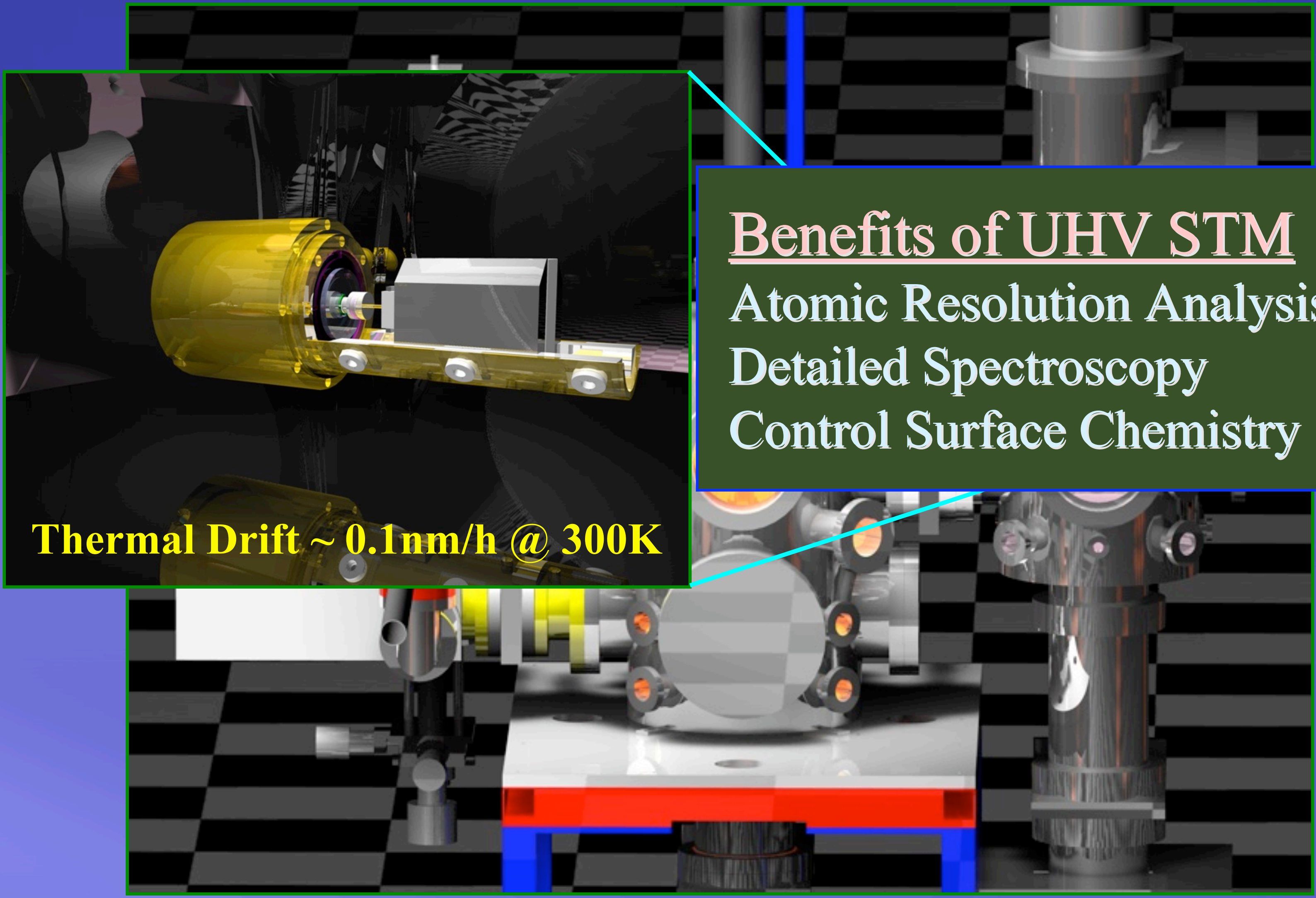
Single Walled Carbon Nanotubes on Si(100)

- Problems with Solution Deposition
- Dry Contact Transfer (DCT) Technique
- Nanotube-Substrate Interactions



Peter Albrecht

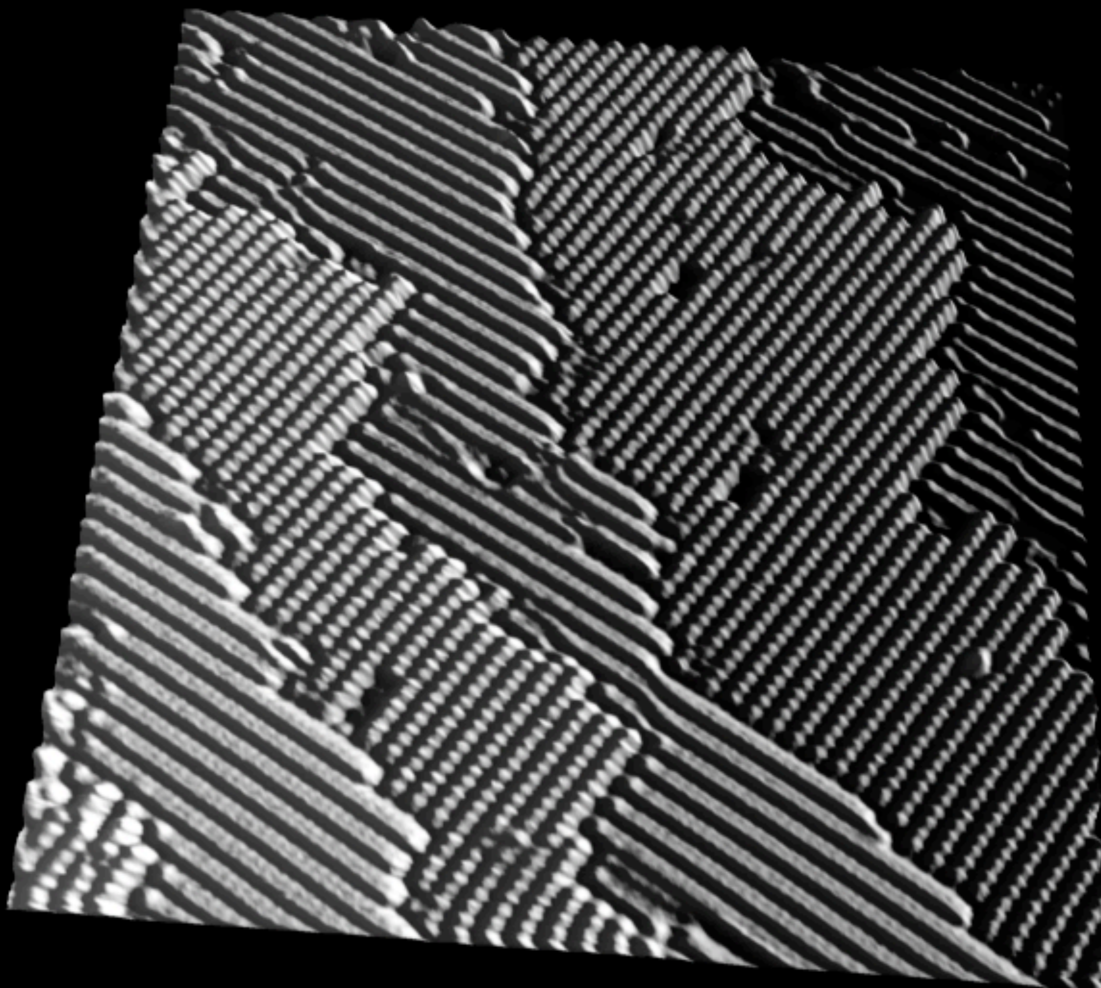
Ultrahigh Vacuum (UHV) Scanning Tunneling Microscopy (STM)



Benefits of UHV STM

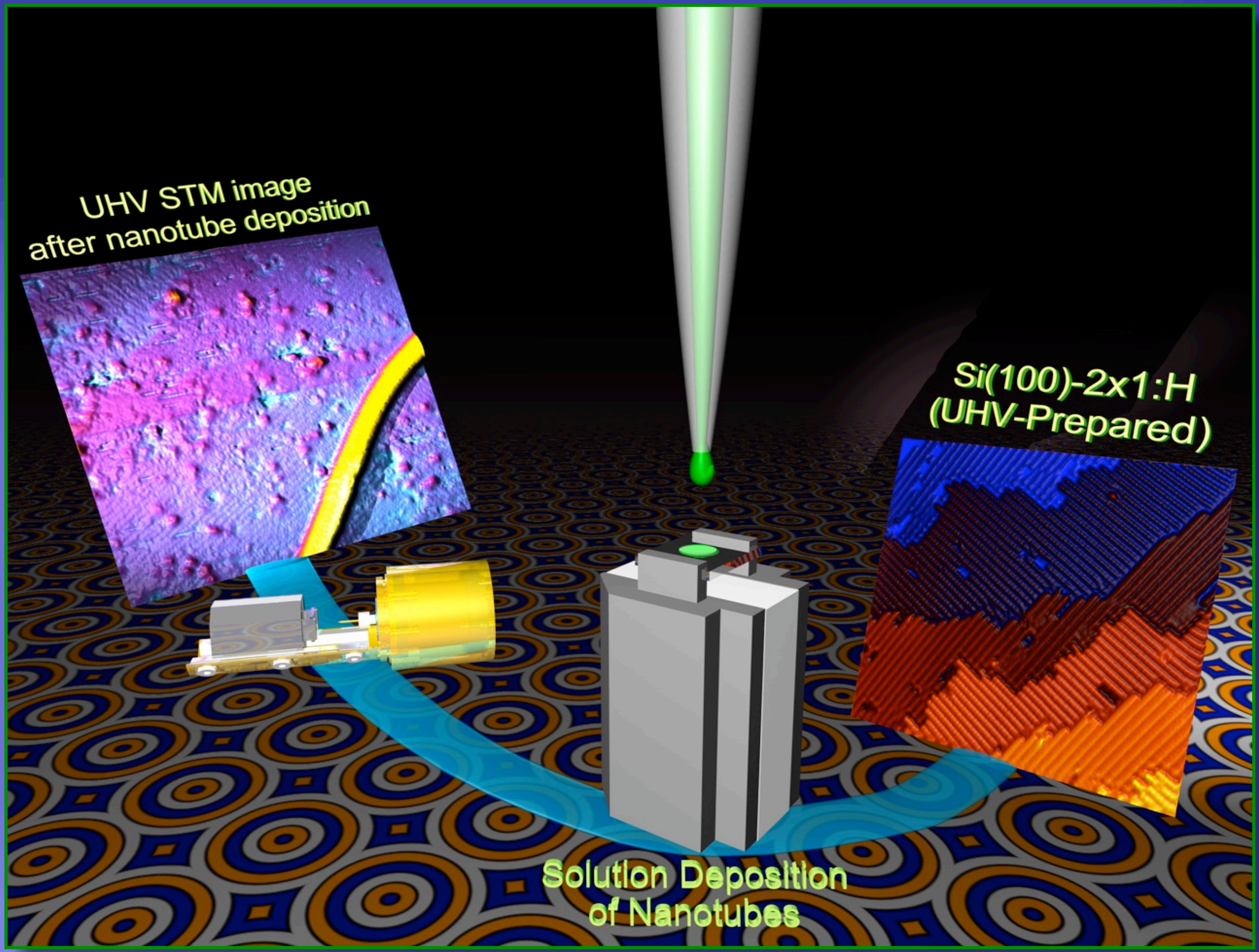
Atomic Resolution Analysis
Detailed Spectroscopy
Control Surface Chemistry

Hydrogen-Passivated Silicon

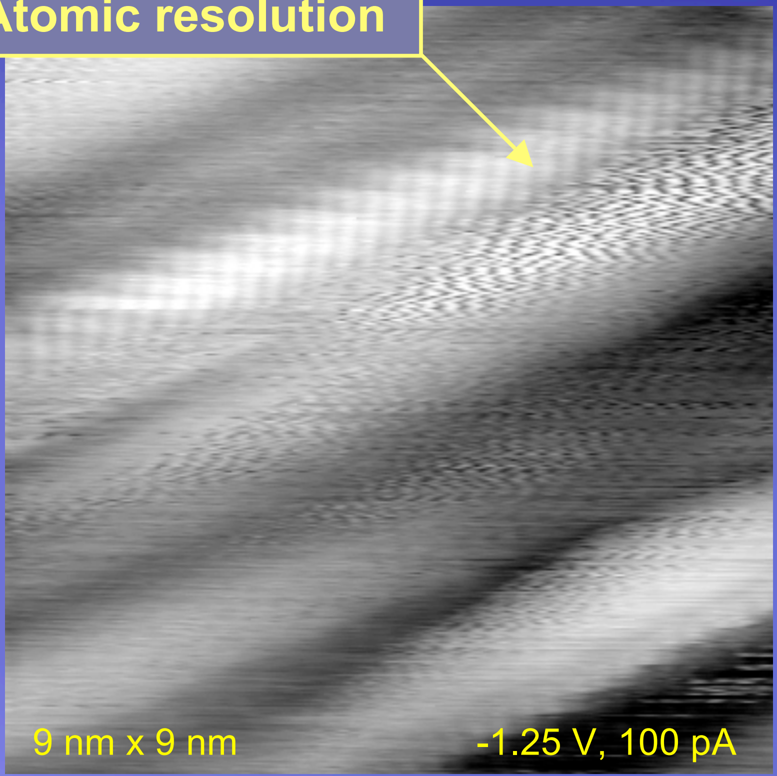


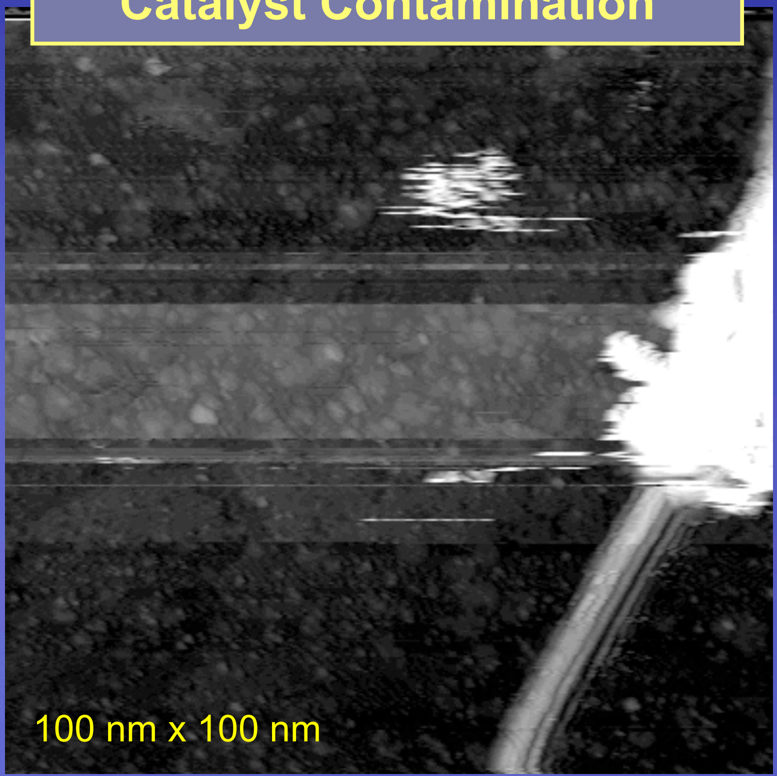
Si(100)-2x1:H

Solution Deposition of SWNTs onto H-Si(100)

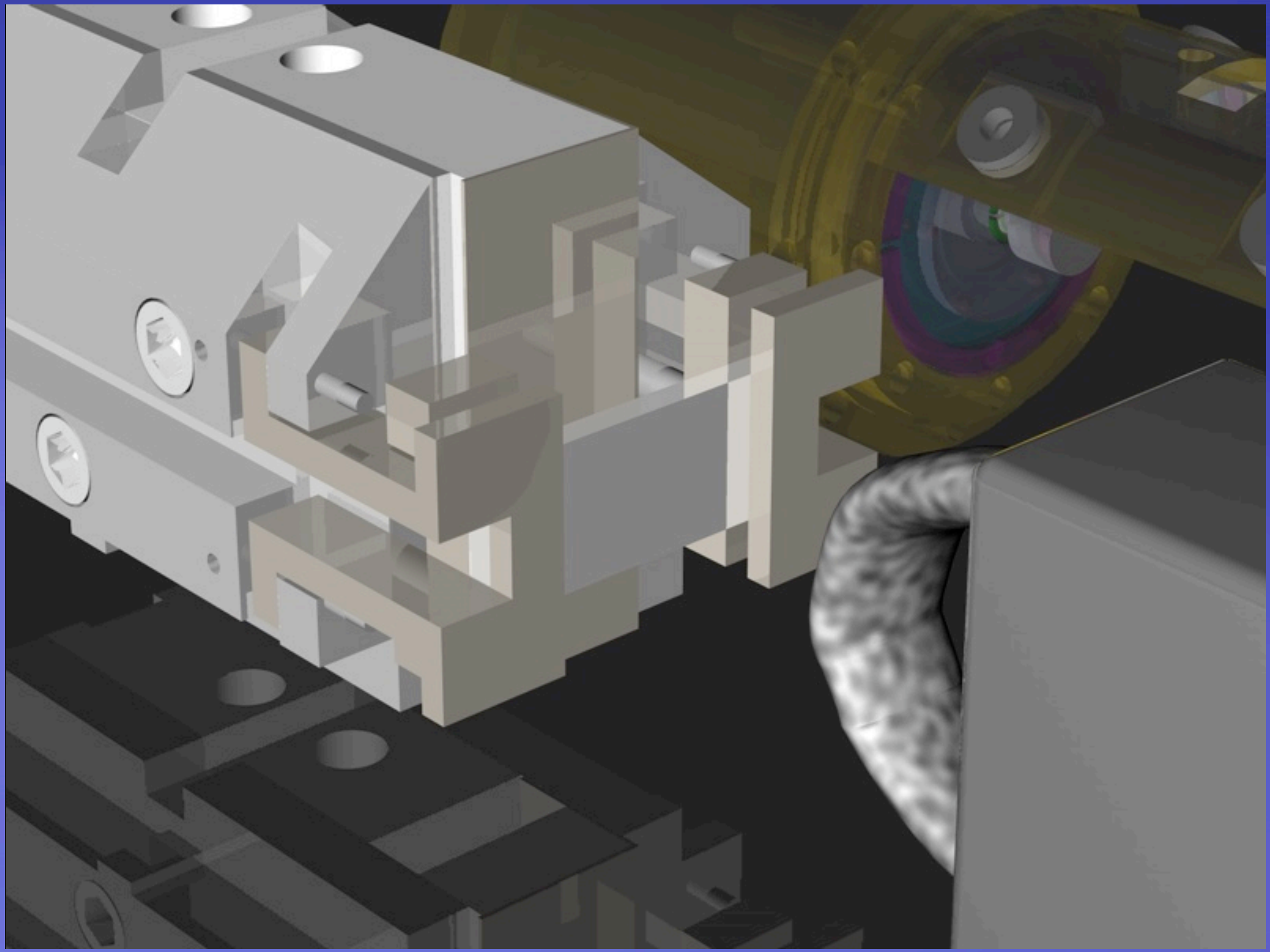


Results of Solution Deposition of SWNTs

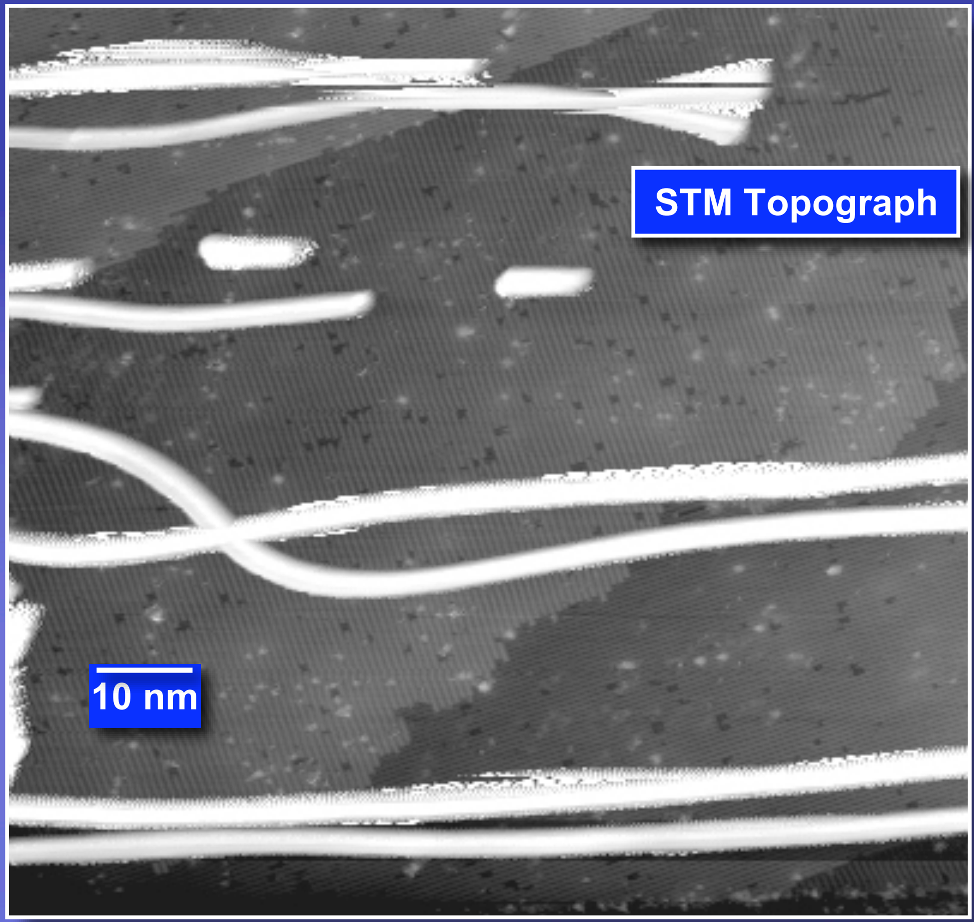




Dry Contact Transfer (DCT) Technique



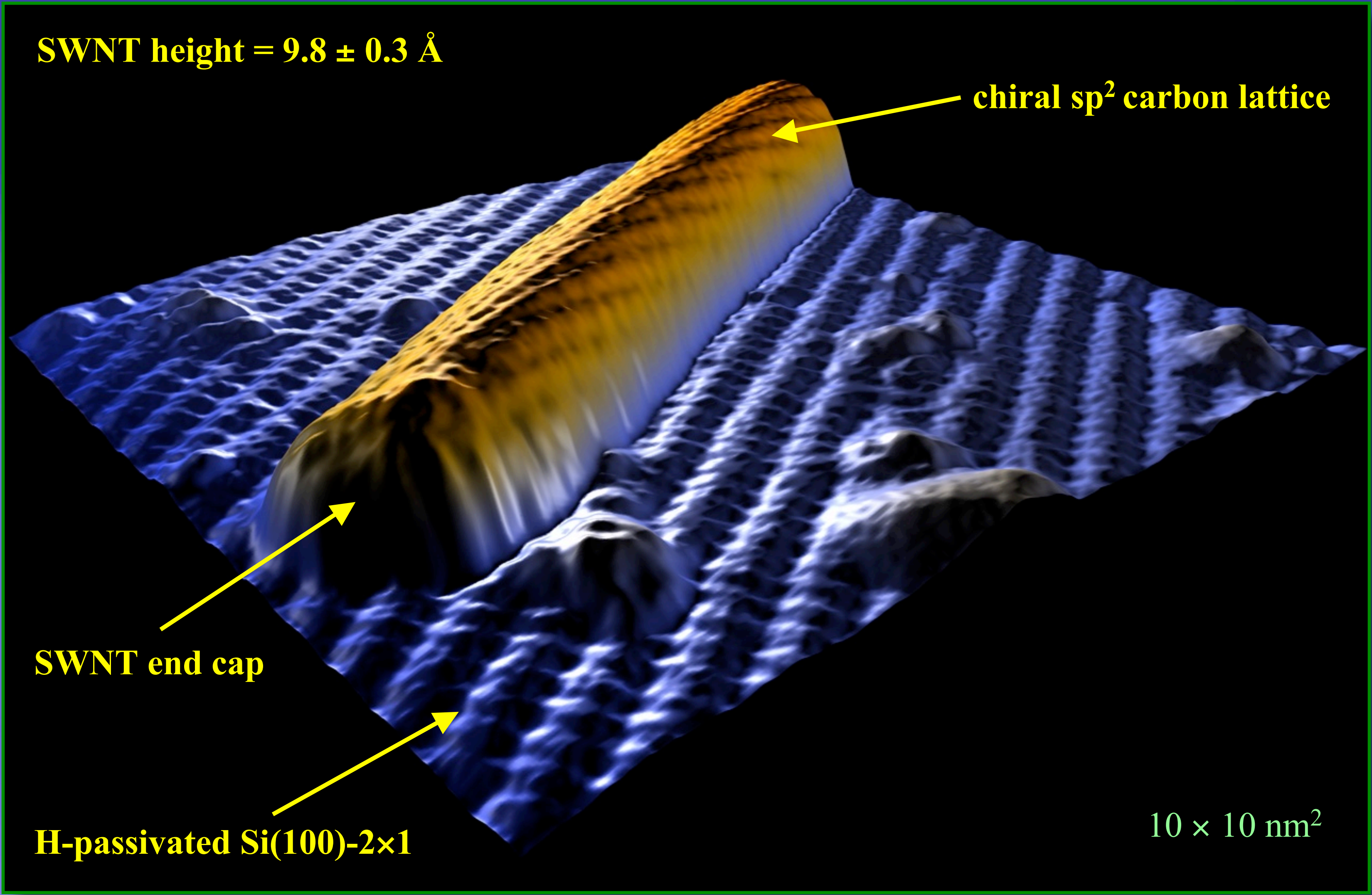
Isolated SWNTs Following DCT



DCT results in the ultra-clean deposition of isolated SWNTs rather than bundles.

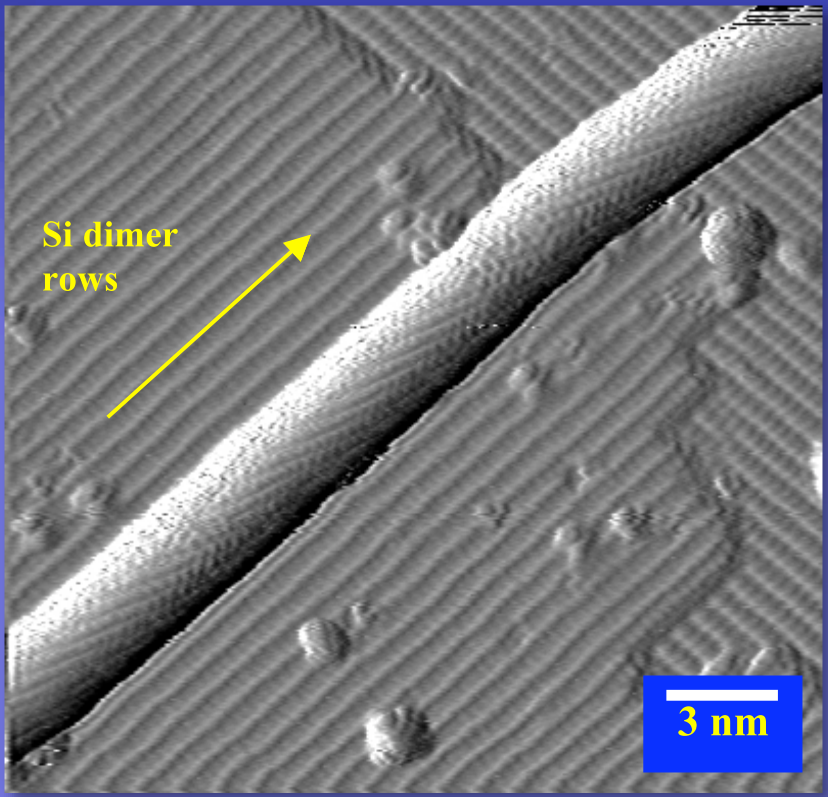
The DCT method can be generalized for the deposition of nearly any nanostructure onto nearly any surface.

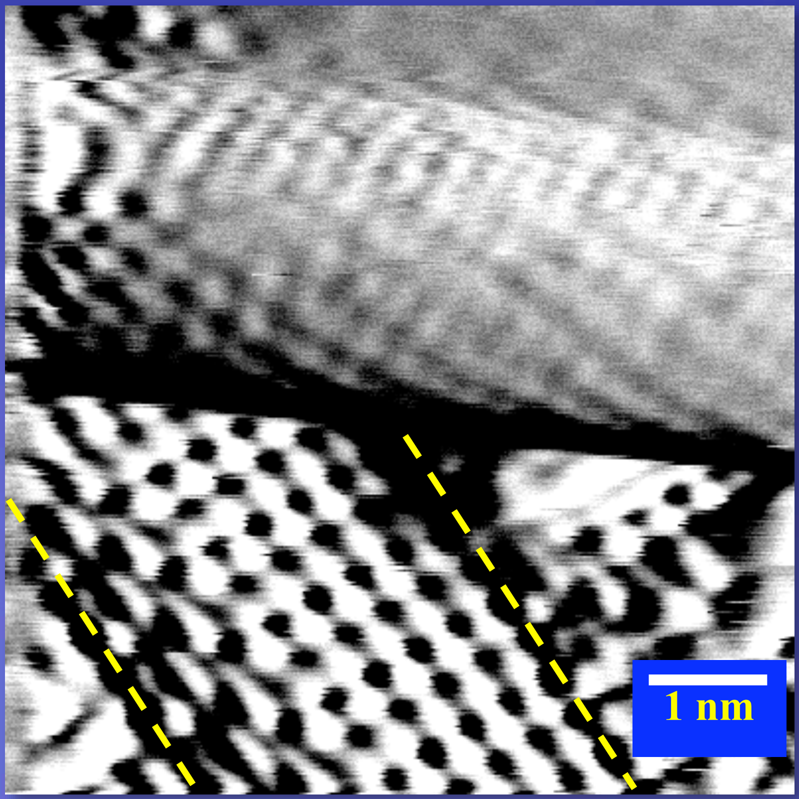
DCT of SWNTs onto Si(100)-2x1:H



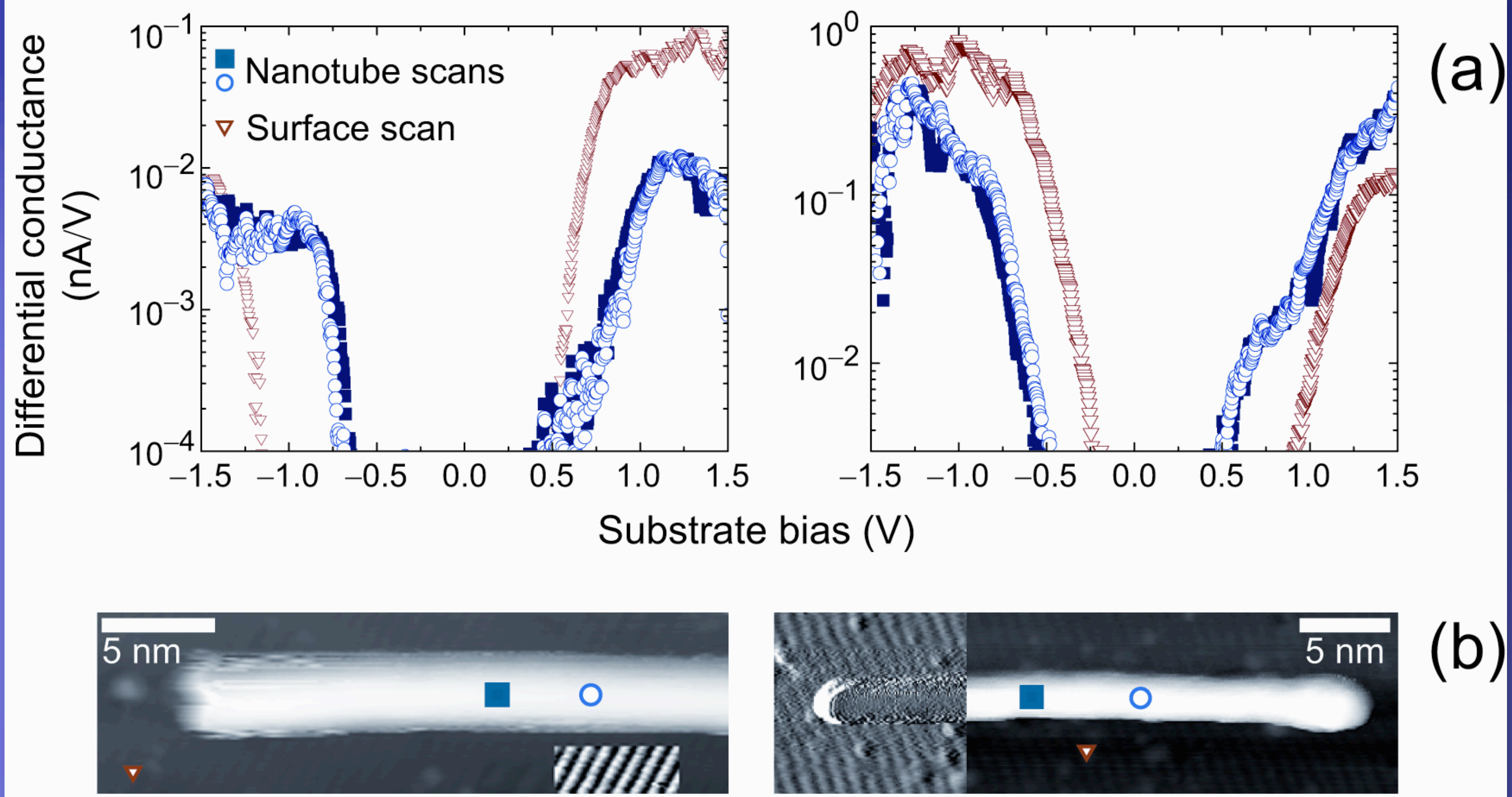
P. Albrecht and J. Lyding, Appl. Phys. Lett. **83**, 5029 (2003).

DCT of SWNTs onto Si(100):H Surfaces





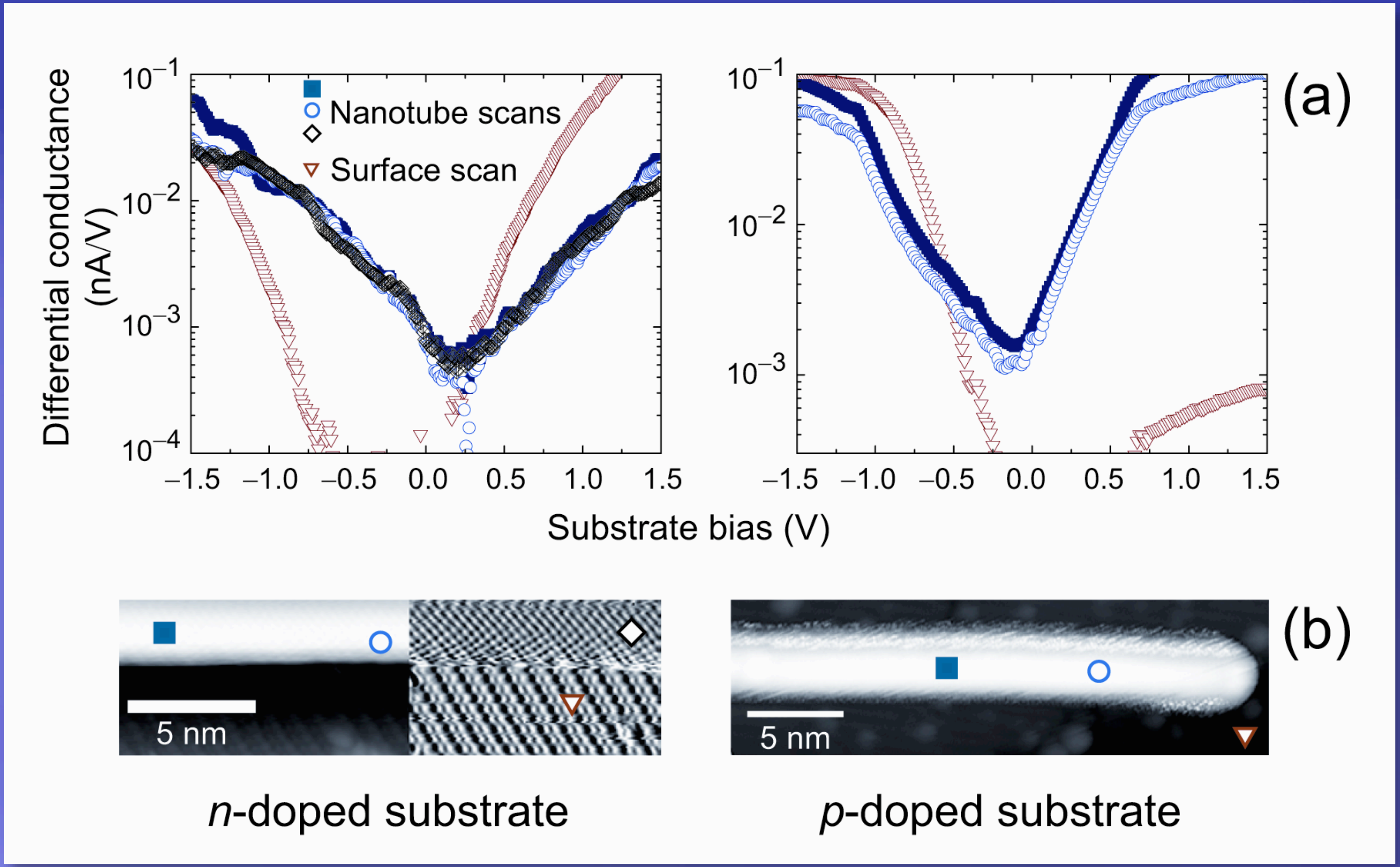
Semiconducting SWNTs on H-Si(100) characterized by STM spectroscopy



n-doped substrate   *p*-doped substrate

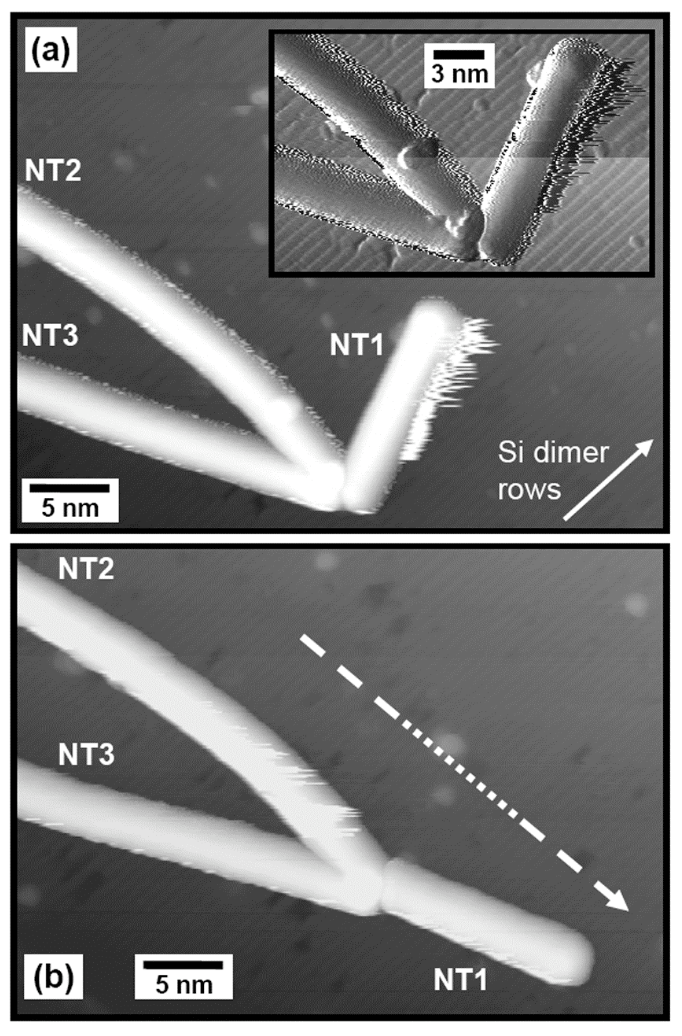
P. M. Albrecht, S. Barraza-Lopez, and J. W. Lyding, *Nanotechnology* **18**, 095204 (2007).

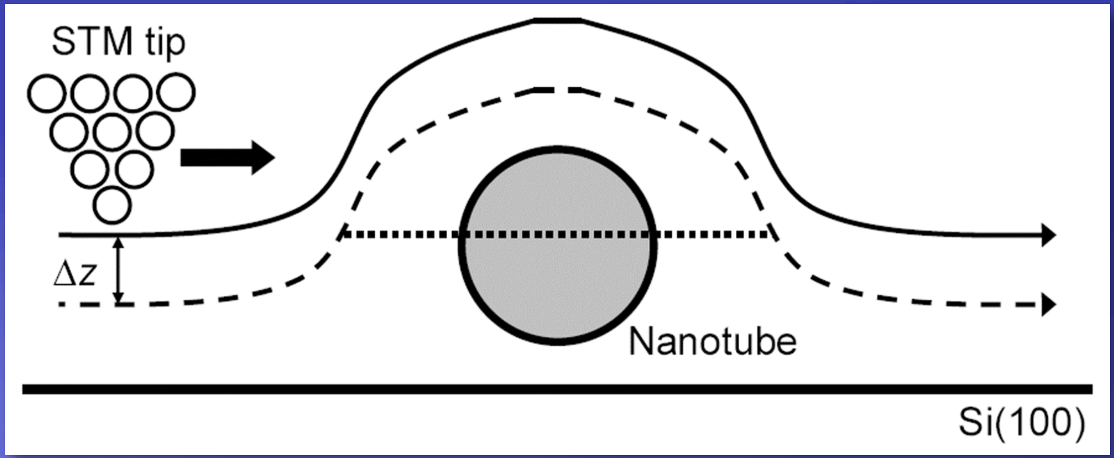
Metallic SWNTs on H-Si(100) characterized by STM spectroscopy



P. M. Albrecht, S. Barraza-Lopez, and J. W. Lyding, *Nanotechnology* **18**, 095204 (2007).

Carbon nanotubes can be precisely manipulated on silicon using the UHV STM

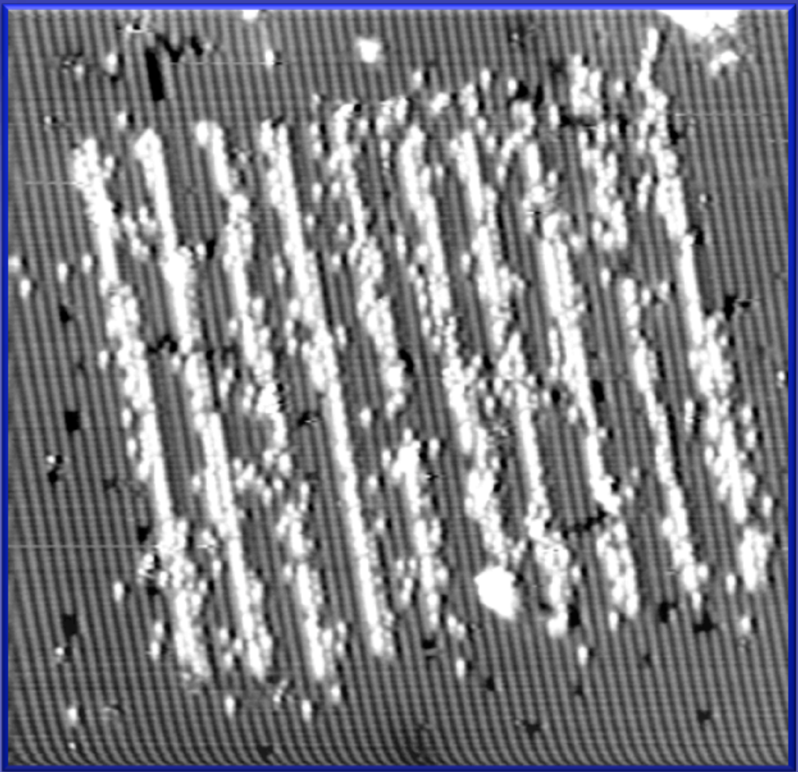




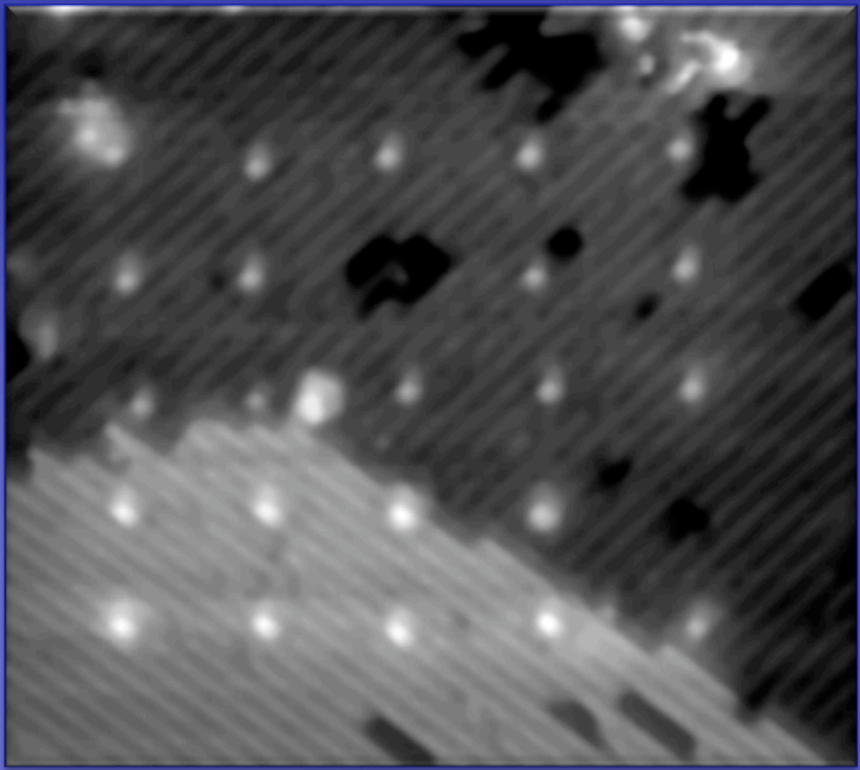
(1) Scan across SWNT with feedback ON and store contour (solid line)
(2) Position tip user-specified Δz (typically 5 Å) closer to the surface
(3) Execute manipulation contour with feedback OFF (dashed line)
(4) Optional: interpolate through the SWNT (dotted line)

P. M. Albrecht and J. W. Lyding, *Small* **3**, 146 (2007).

Nanopatterning H-Si(100)

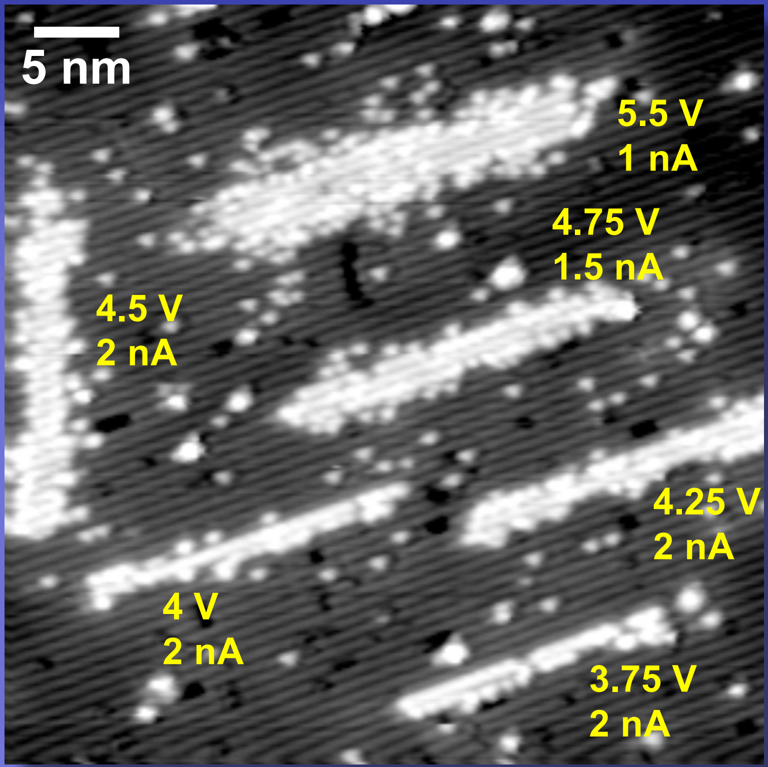


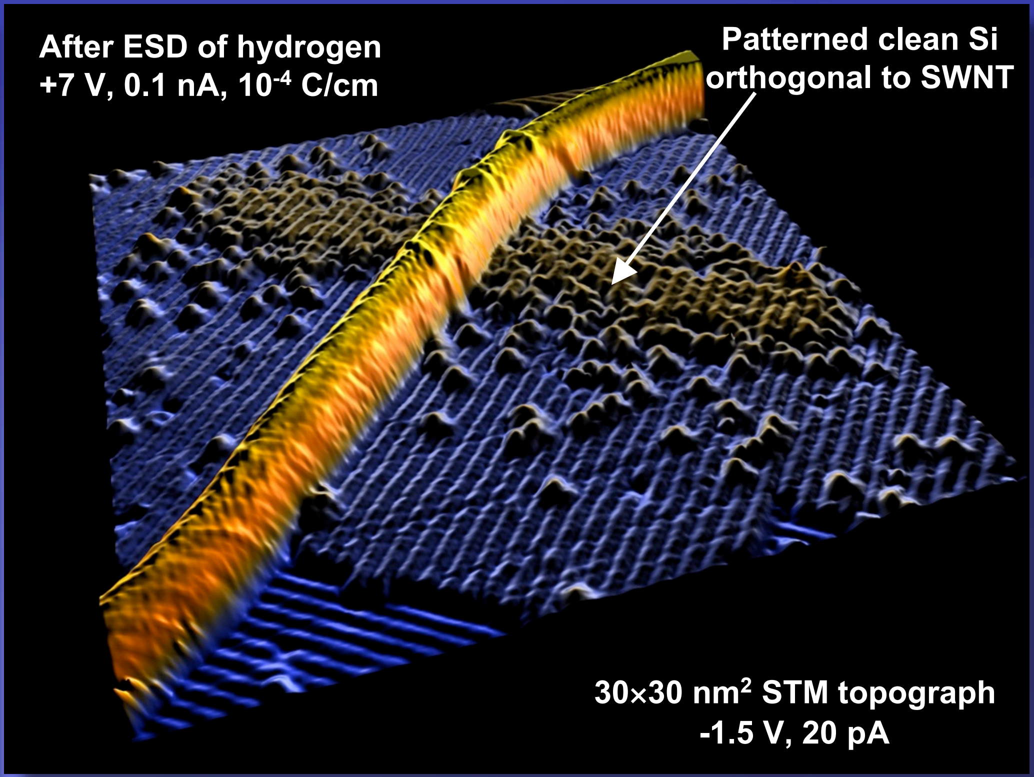
Lyding et al., Appl. Phys. Lett. **64**, 2010 (1994)



Hersam et al., Nanotechnology **11**, 70 (2000)

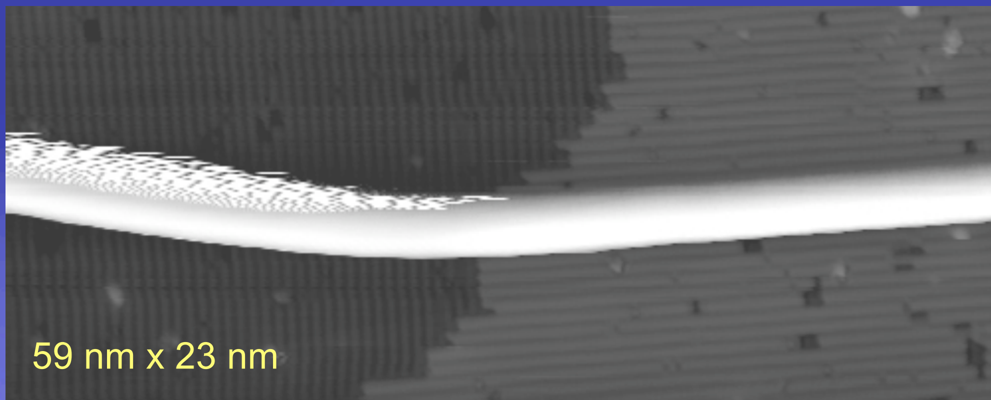
Controlling Nanotube – Substrate Interactions:
STM Nanolithography



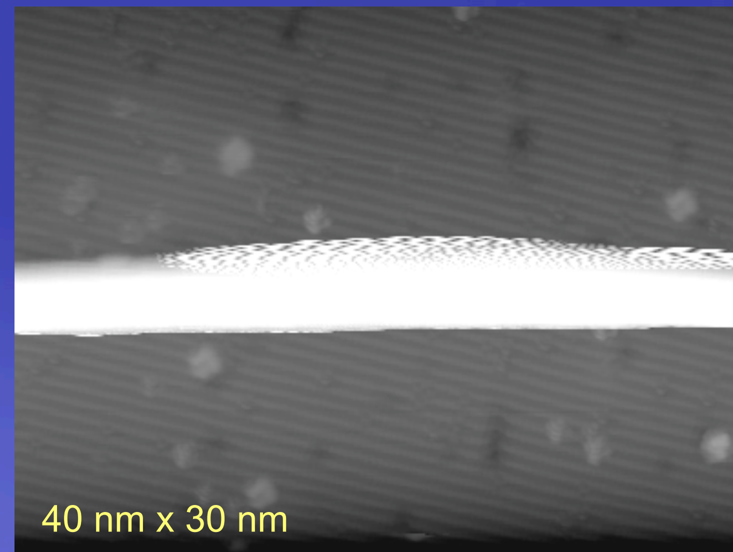


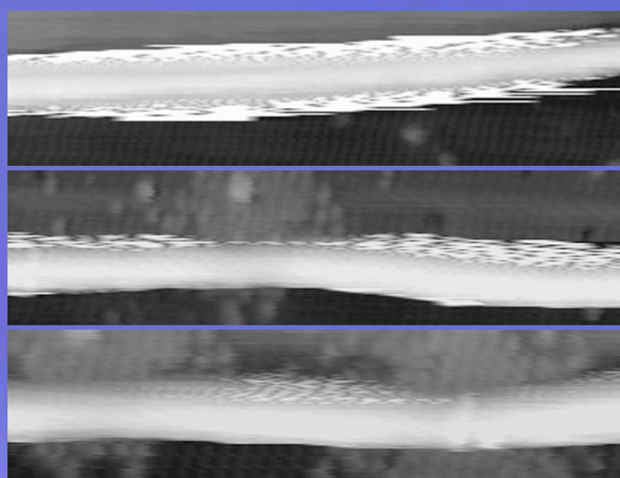
Nanotube-Substrate Interaction

H-Passivated vs Clean Si(100)

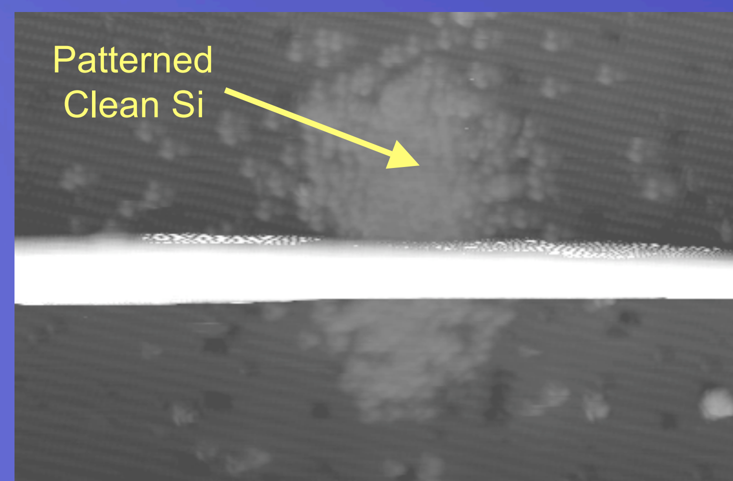


Nanotube Instability Depends on Alignment with Si Lattice

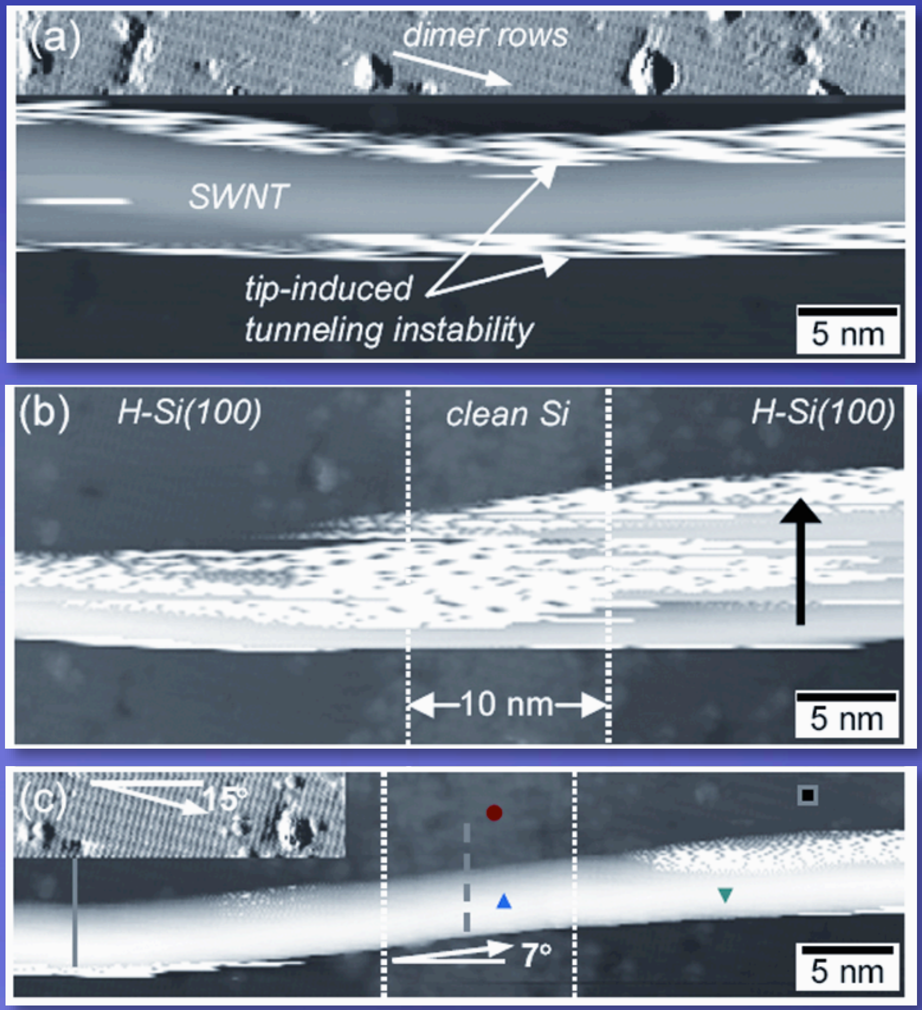




Clean Si Stabilizes Nanotube

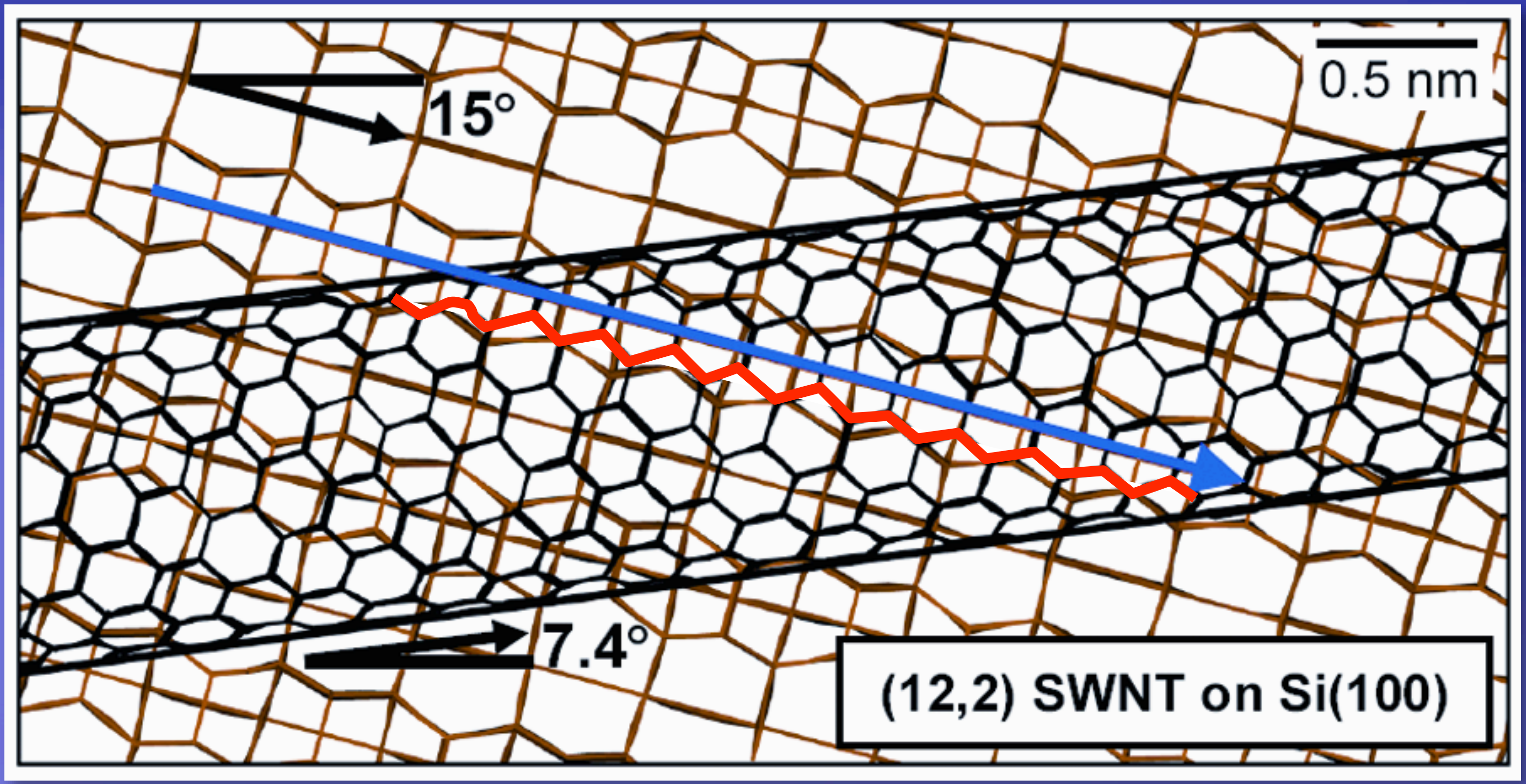


Preferential orientation of a semiconducting tube on STM-patterned H-Si(100)



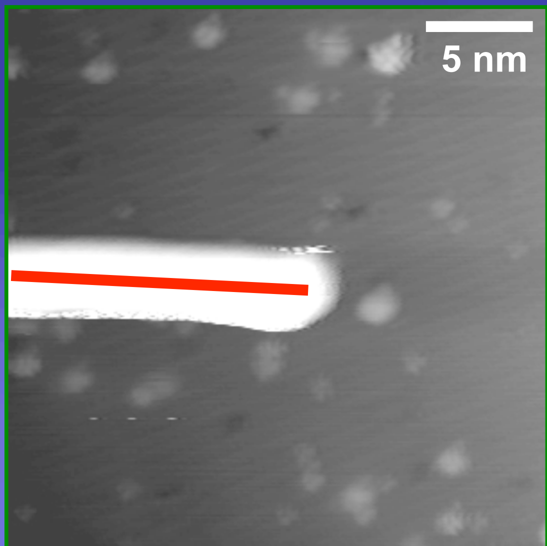
P. M. Albrecht, S. Barraza-Lopez, and J. W. Lyding, *Small* **3**, 1402 (2007).

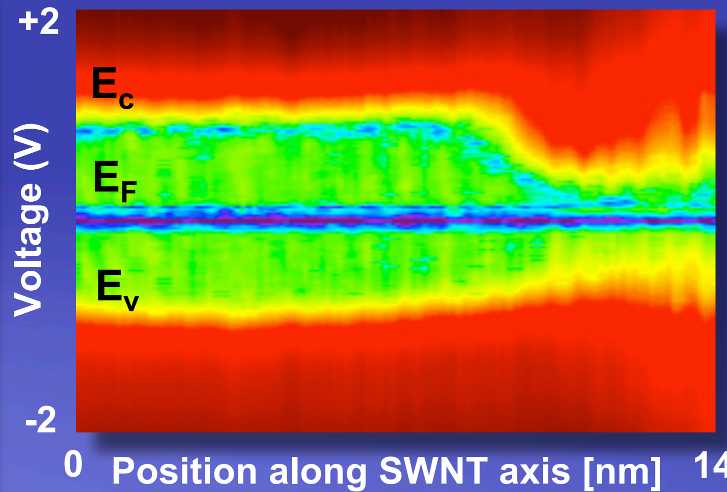
SWNT zigzag symmetry aligns parallel to Si dimer rows



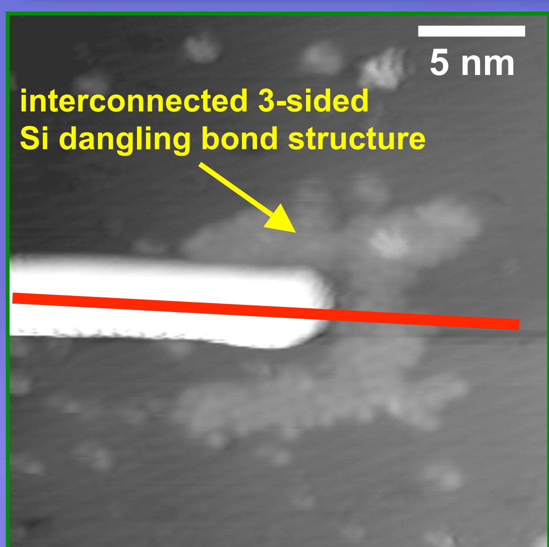
P. M. Albrecht, S. Barraza-Lopez, and J. W. Lyding, *Small* **3**, 1402 (2007).

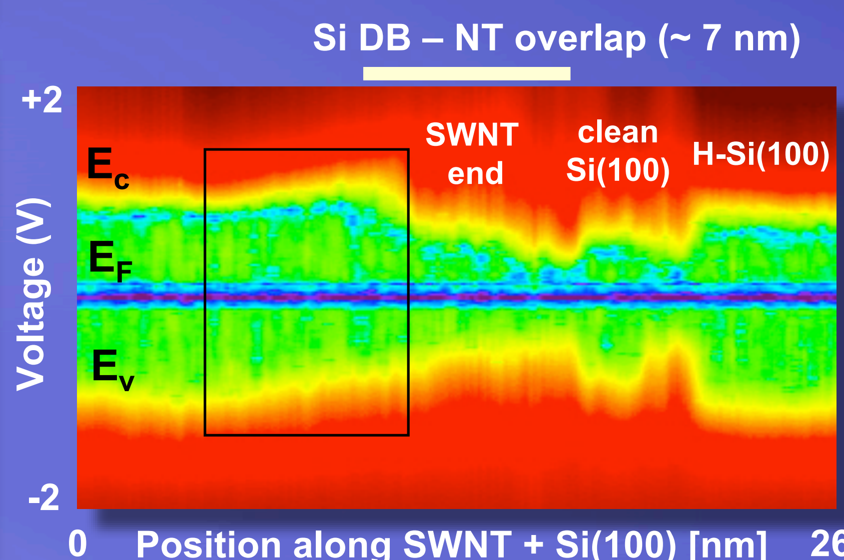
Nanotube Electronic Structure: Influence of Local Charge





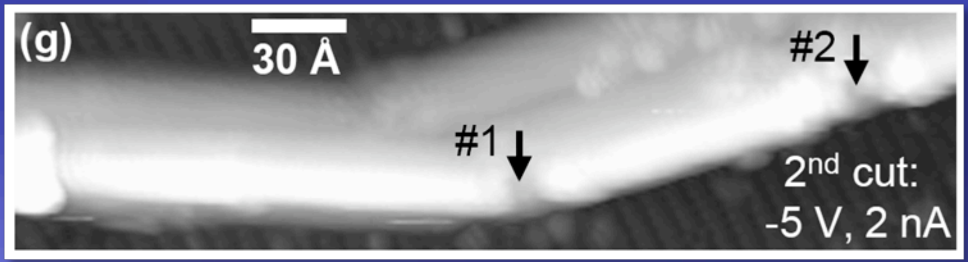
- **Before patterning**
- Abrupt E_c shift ~5 nm from the end of SWNT
- Semiconducting gap closes at the SWNT end

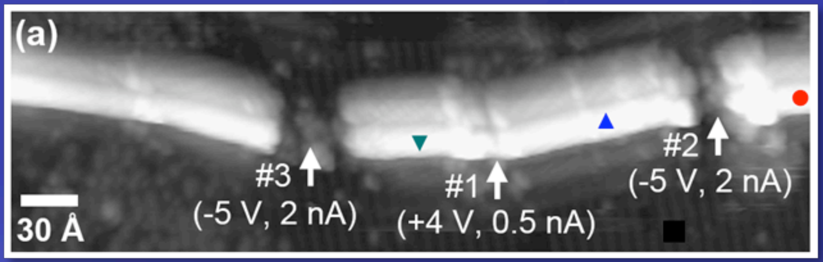


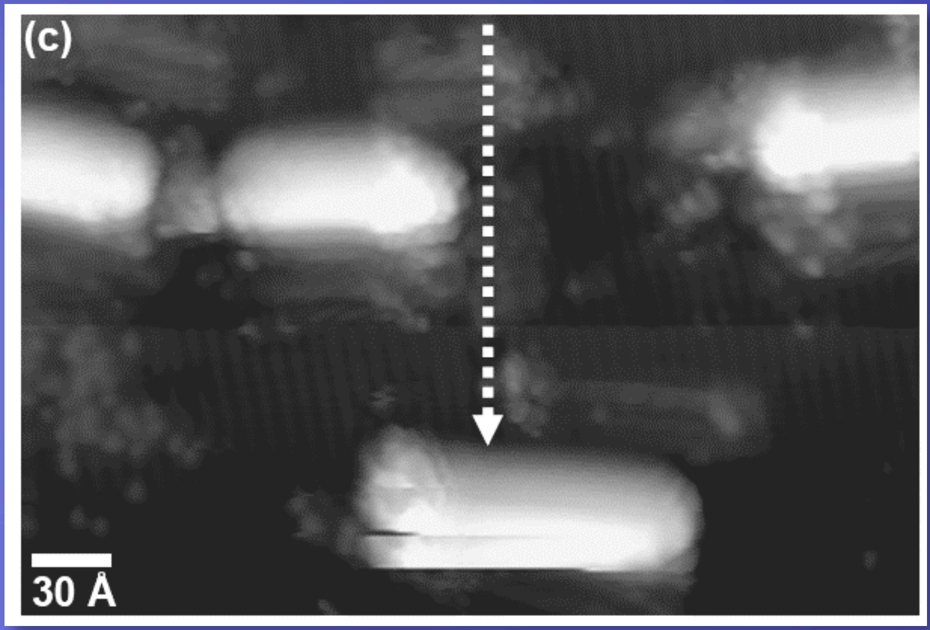


- **After patterning**
- Upward band bending within SWNT
- Band bending suggests (-) charged Si dangling bonds in proximity

Individual SWNTs can be cut with the STM under feedback control





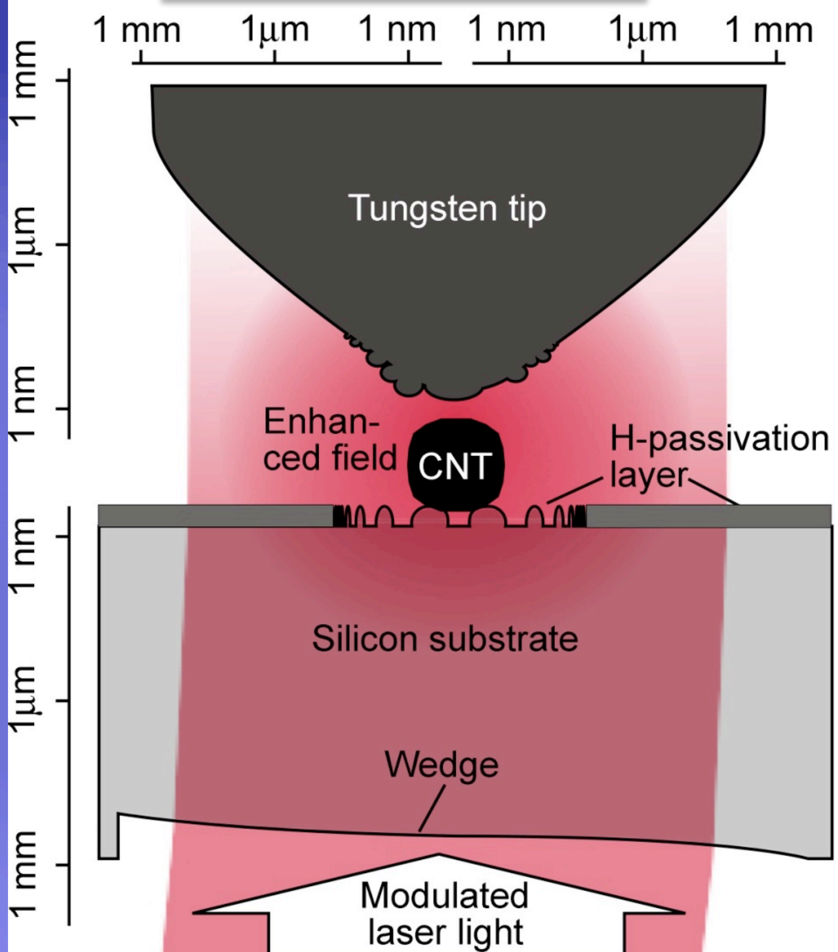


P. M. Albrecht and J. W. Lyding, *unpublished.*

Single molecule absorption spectroscopy detected by STM

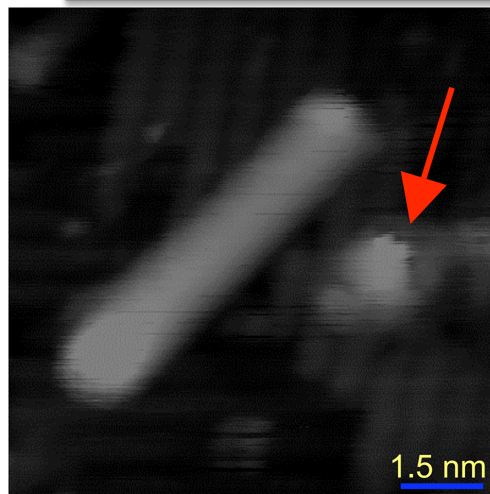
Erin Carmichael, Josh Ballard, Dongxia Shi, Greg Scott, Martin Gruebele

Rear illumination and transparent substrate



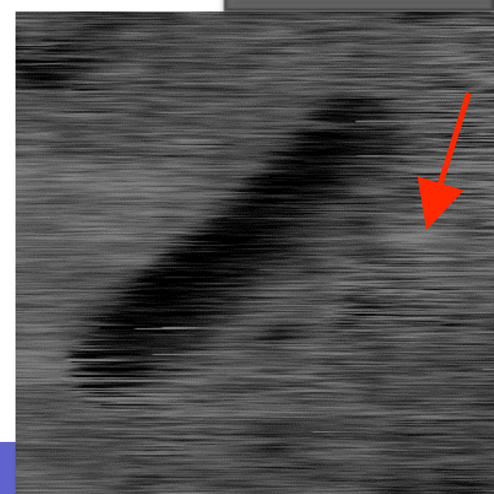
Carmichael et al., J. Phys. Chem. C (2007)

CNT on Si(100)2x1:H surface



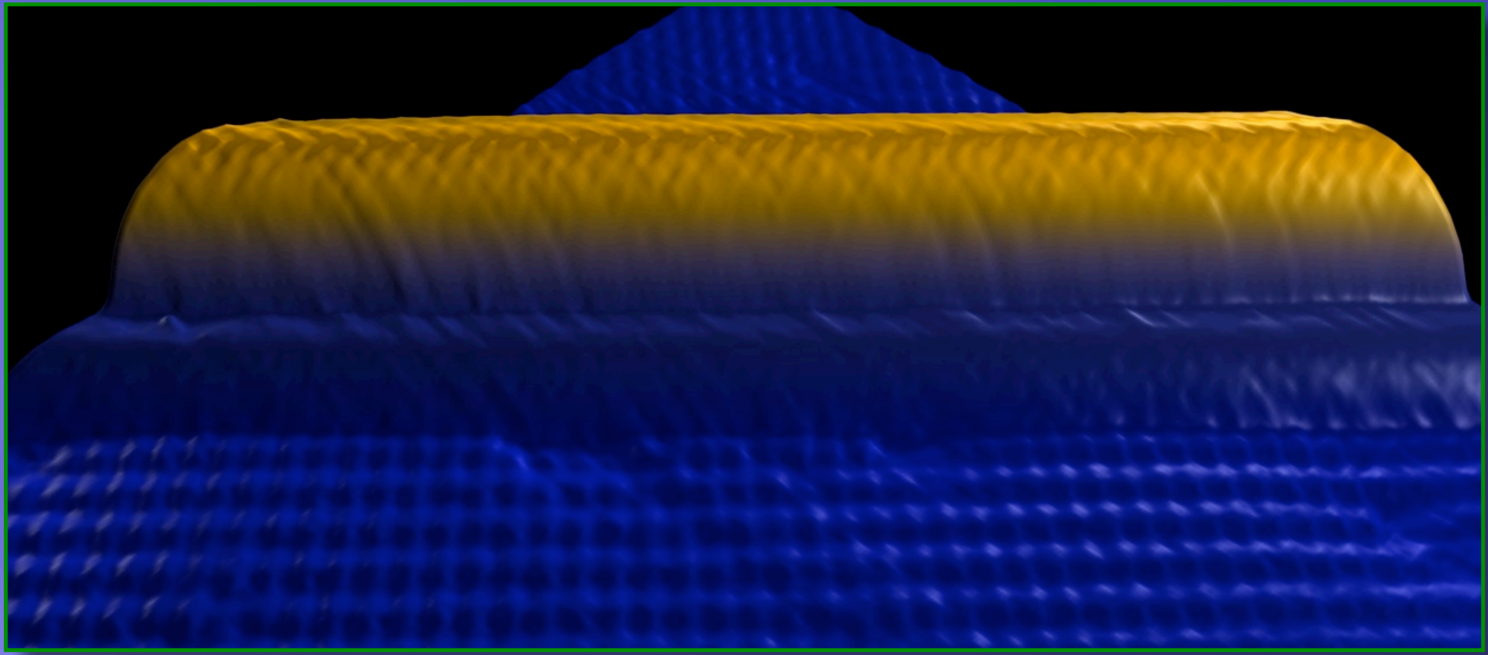
Topographic Signal (STM)

Absorption Signal



SWNTs on UHV-Cleaved GaAs(110) and InAs(110)

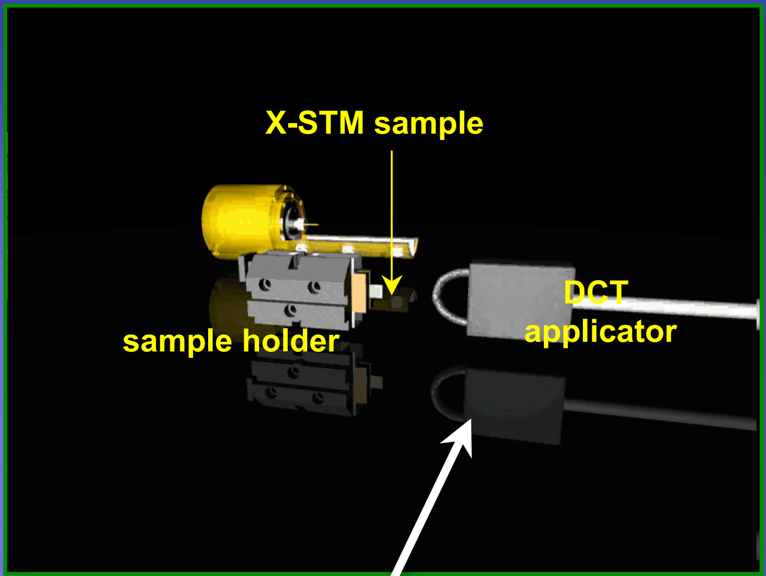
- Nanotube-Substrate Alignment
- NT-NT Metal-Semiconductor Junction
- Nanotube-Substrate Electronic Interactions

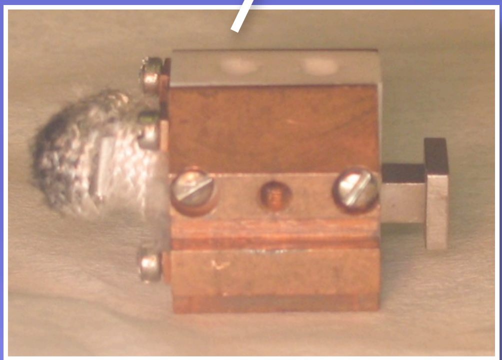


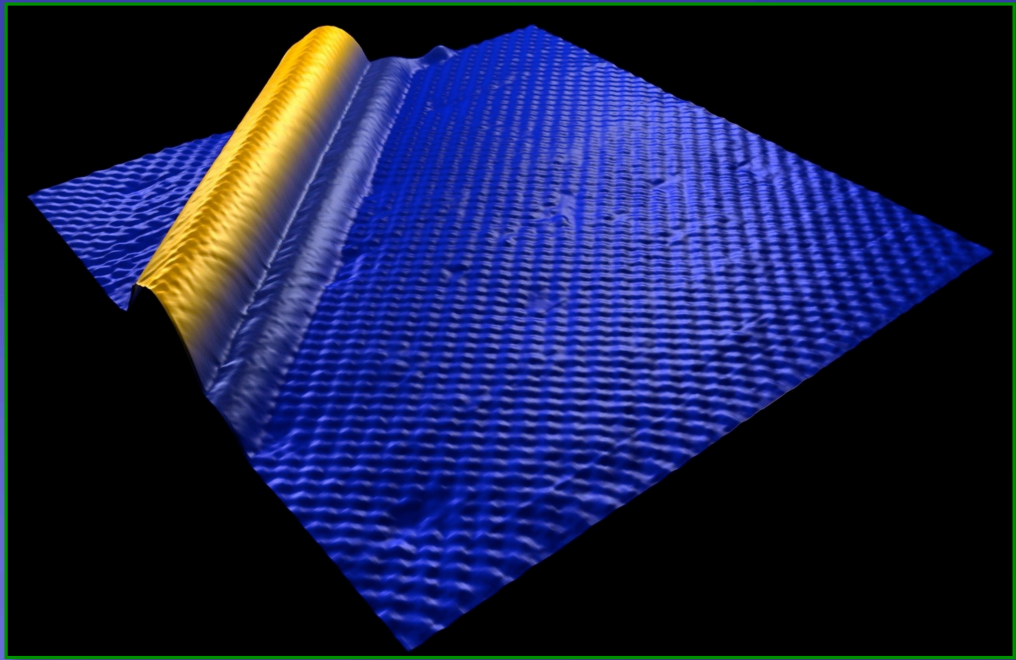
Laura Ruppalt

DCT of SWNTs onto the III-V(110) Surface

DCT Process



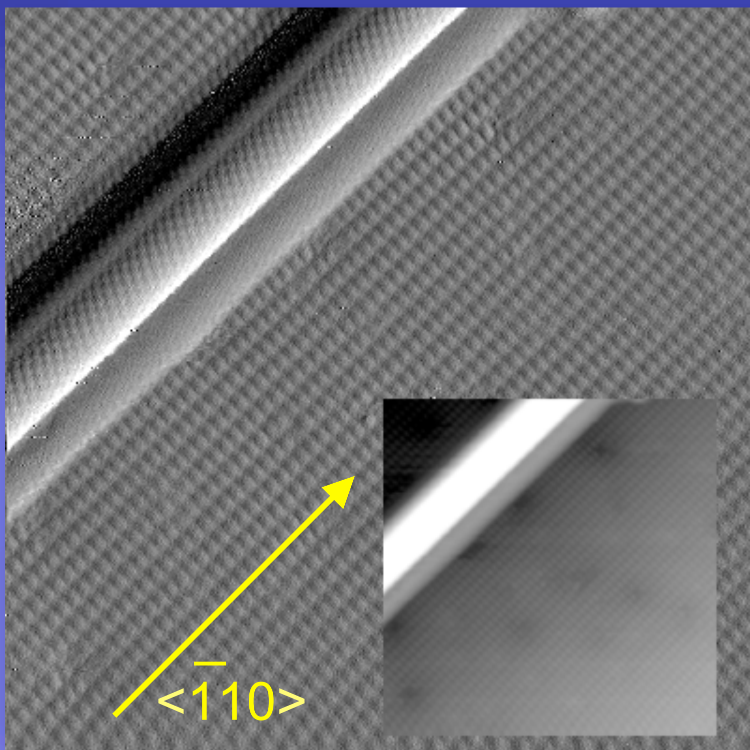




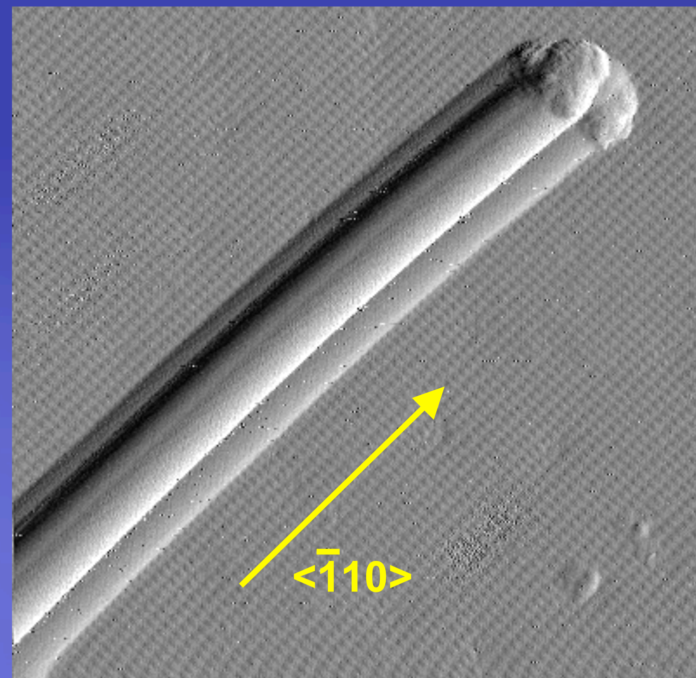
19.5 nm, 15 pA, 1.7 V

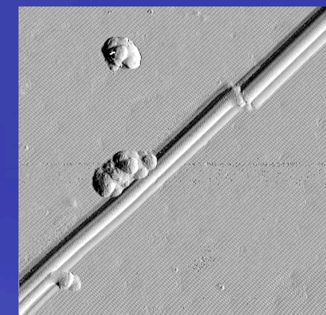
L. B. Ruppalt, P. M. Albrecht and J. W. Lyding, JVST B**22**, 2005 (2004).

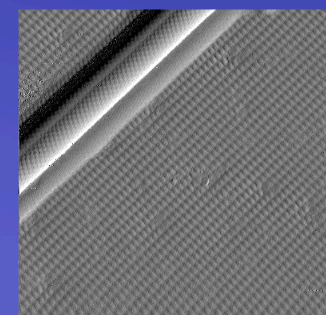
SWNTs Preferentially Align Along Lattice Rows

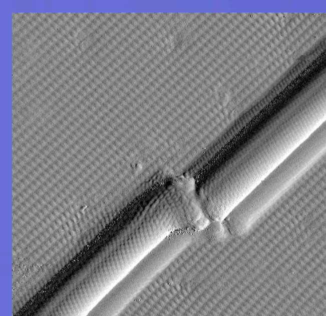


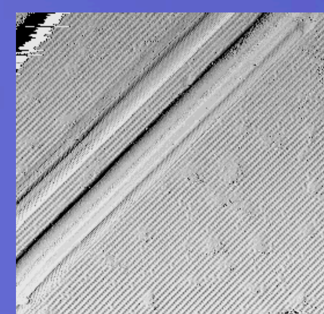
19.5 nm, 15 pA, 1.7 V

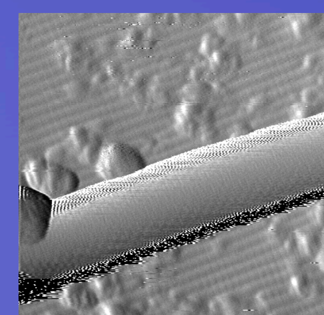




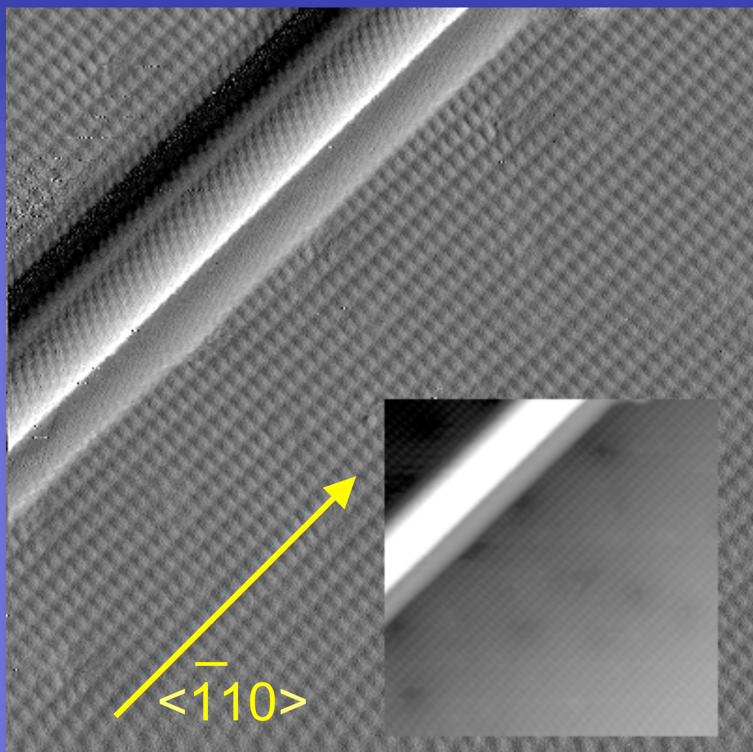




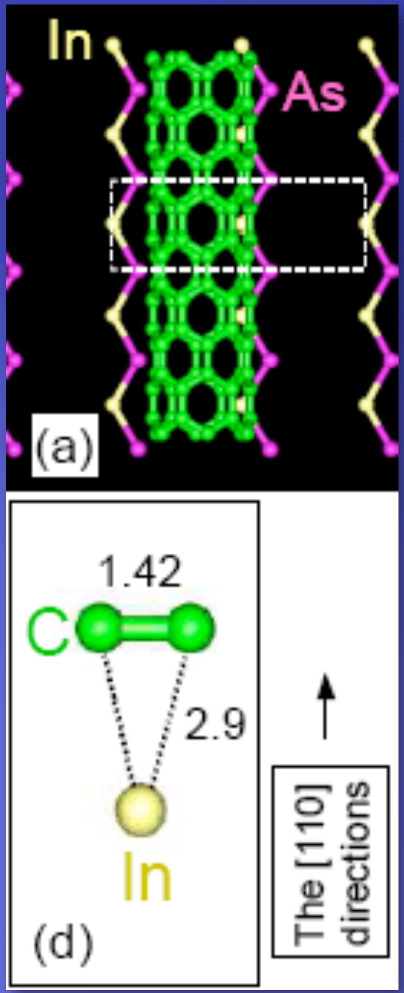




SWNTs Preferentially Align Along Lattice Rows



19.5 nm, 15 pA, 1.7 V

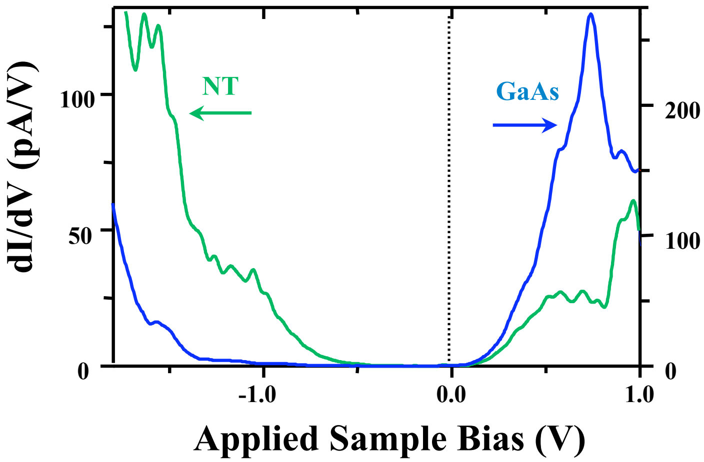


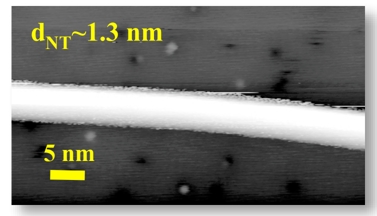
Yong-Hyun Kim, M. J. Heben, and S.B. Zhang, *PRL*, **92,** 176102-1 –4 (April 2004)

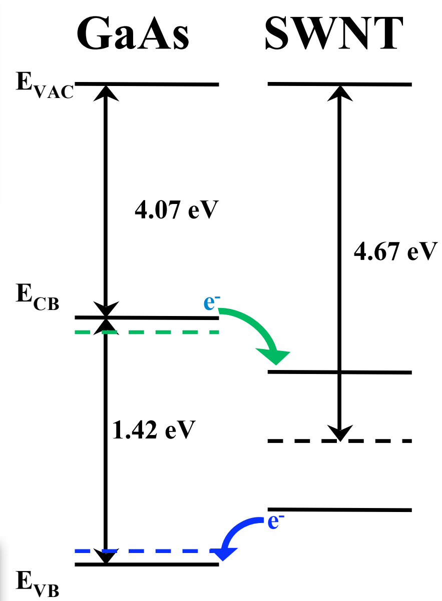
SWNTs on GaAs(110): Substrate-Induced NT Doping

SWNTs on GaAs(110)

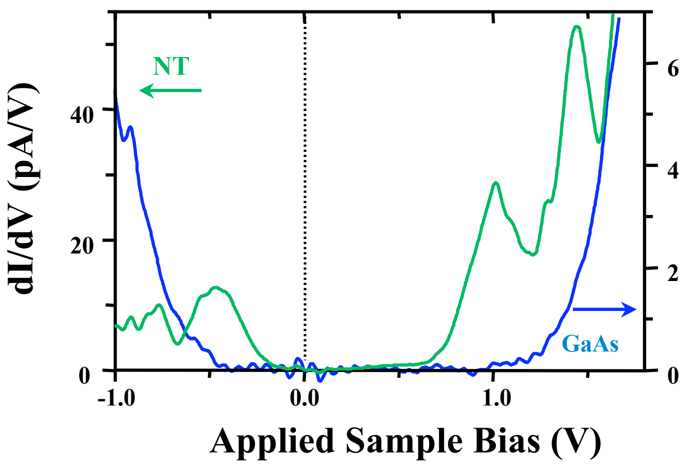
SWNT on n-GaAs

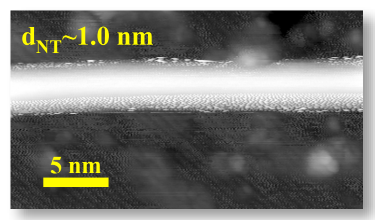






SWNT on p-GaAs

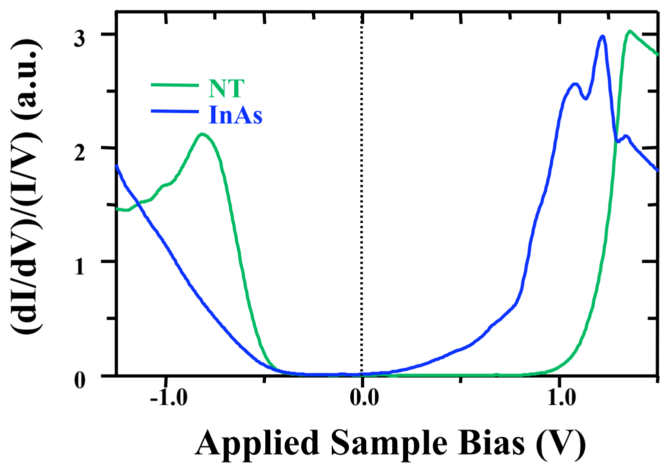


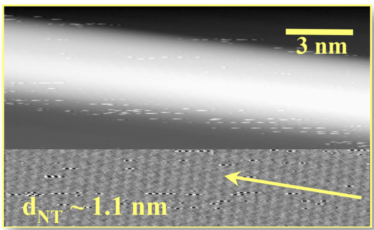


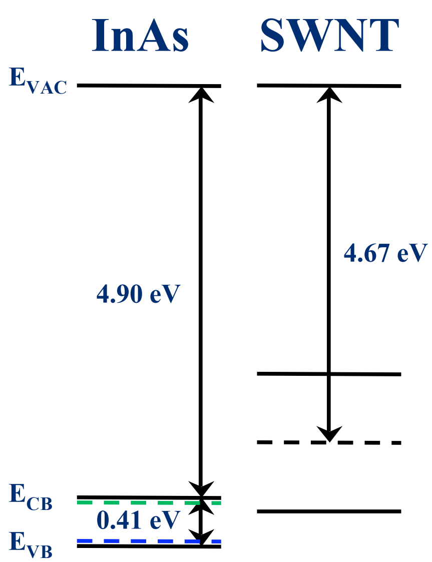
L.B. Ruppalt and J.W. Lyding, *Nanotechnology* **18**, 215202 (2007)

SWNTs on InAs(110): Substrate-Induced NT Doping

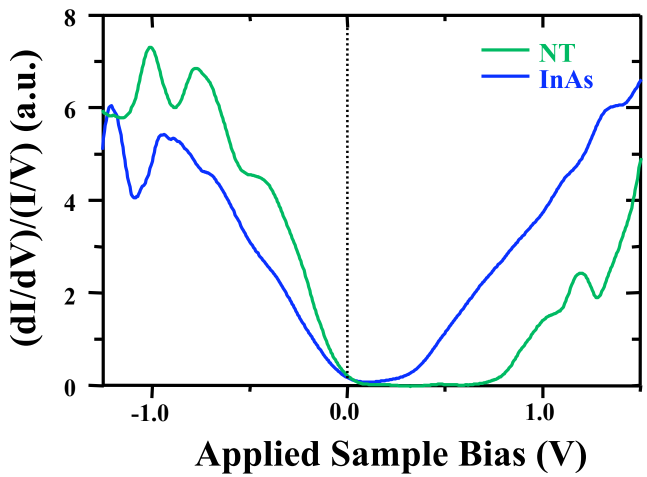
SWNT on n-InAs

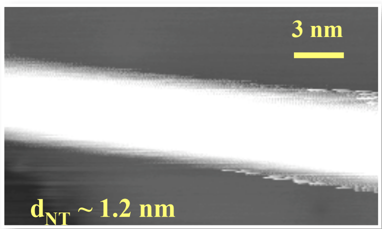






SWNT on p-InAs

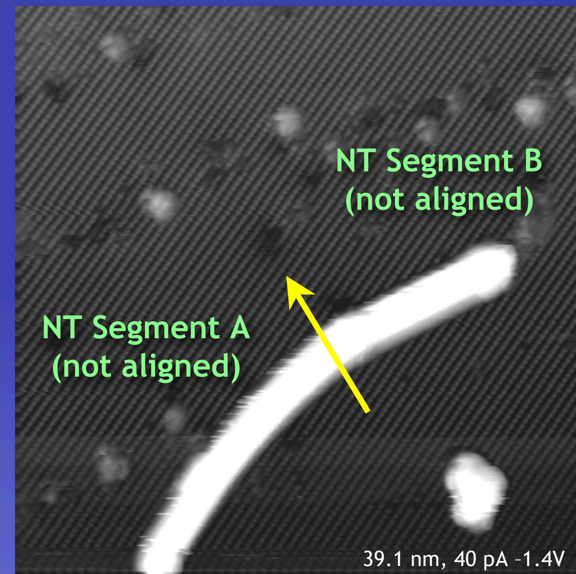


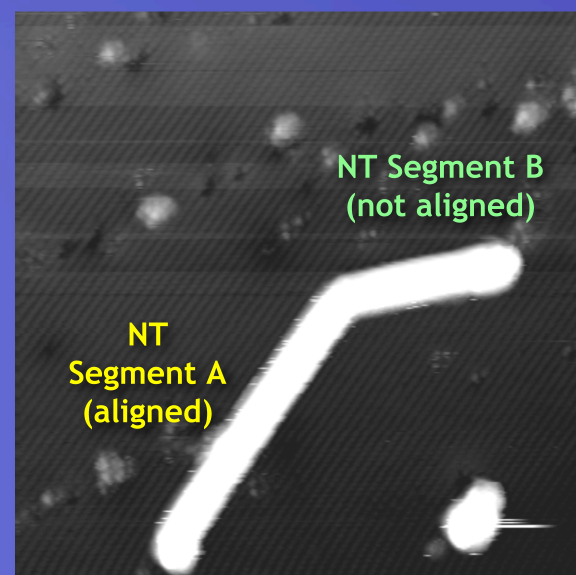


L.B. Ruppalt and J.W. Lyding, *Nanotechnology* **18**, 215202 (2007)

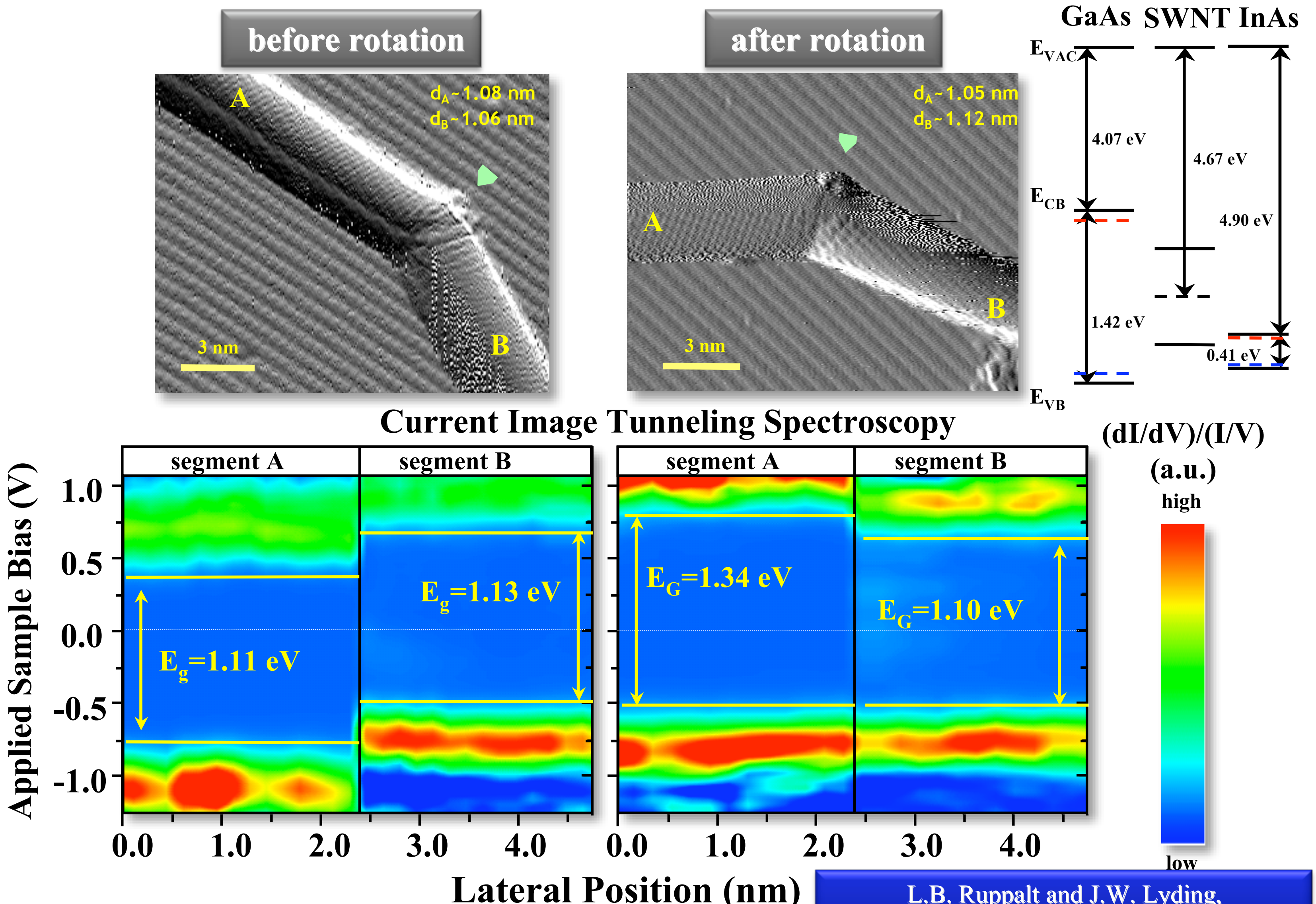
SWNTs on InAs: Orientation-Dependent Effects

L.B. Ruppalt and J.W. Lyding, *Nanotechnology* **18**, 215202 (2007)



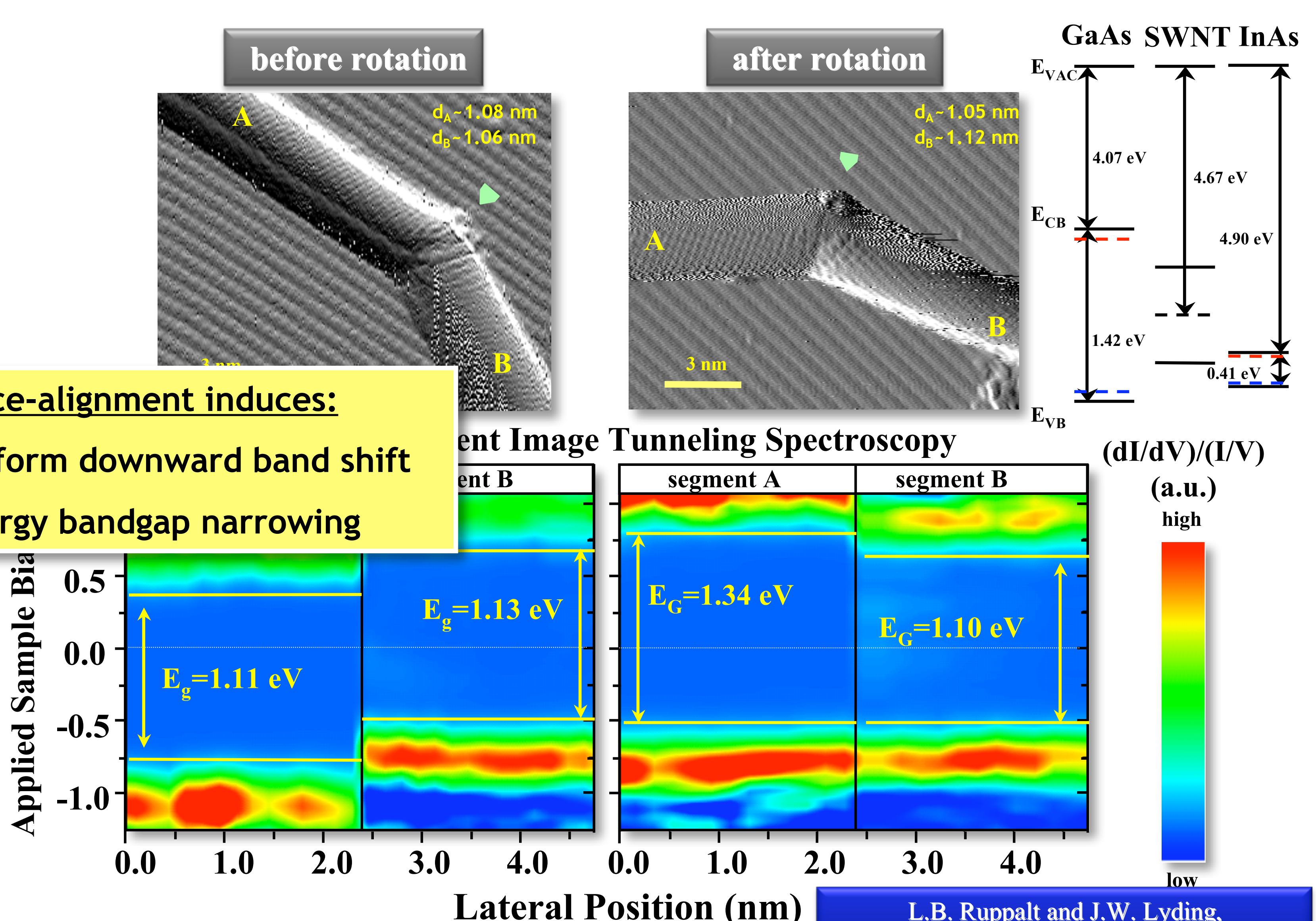


SWNTs on InAs: Orientation-Dependent Effects



L.B. Ruppalt and J.W. Lyding, *Nanotechnology* **18**, 215202 (2007)

SWNTs on InAs: Orientation-Dependent Effects

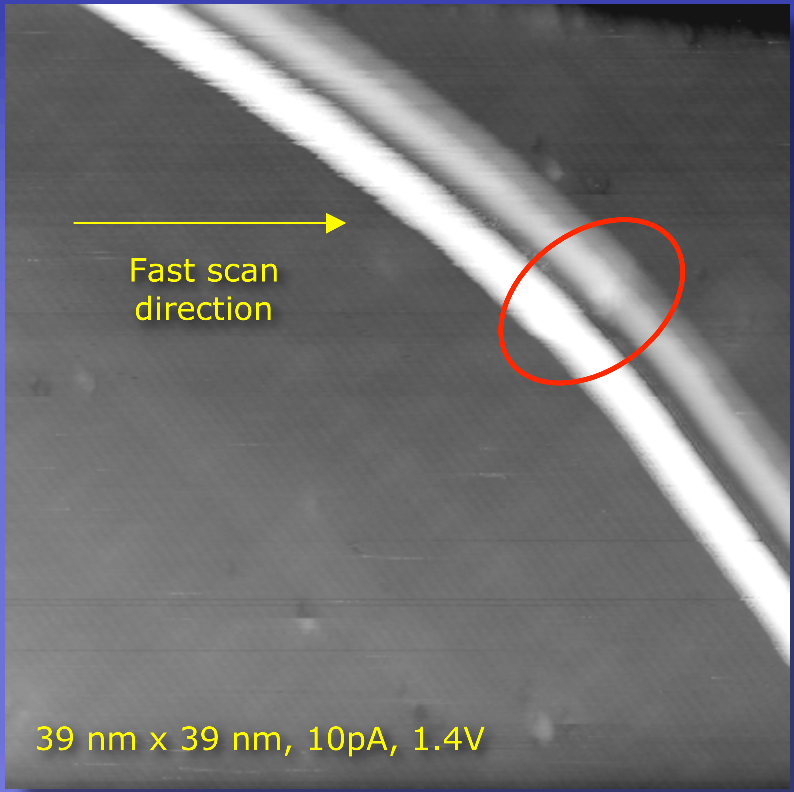


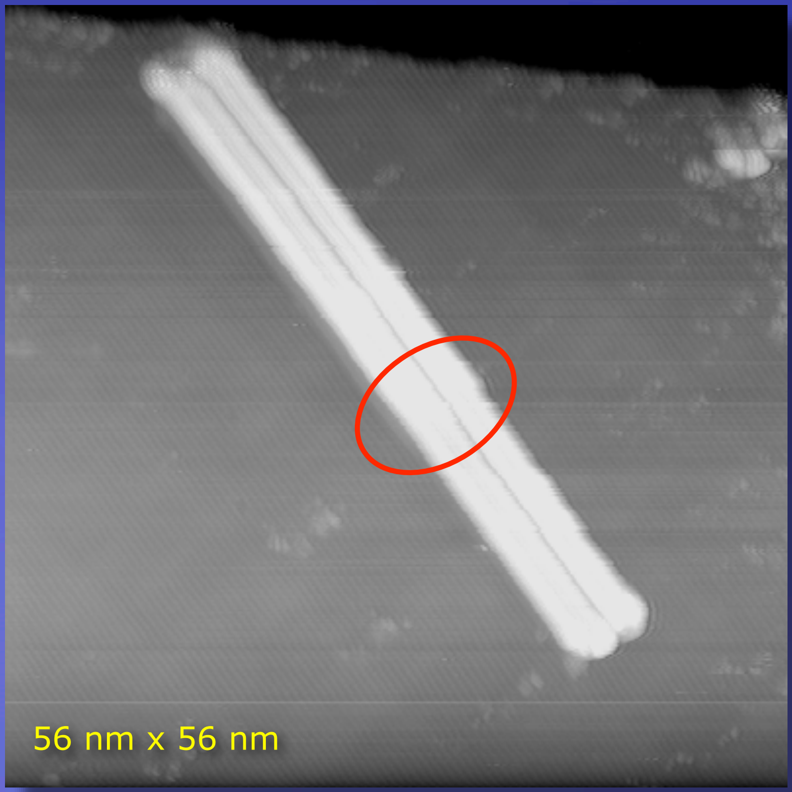
Lattice-alignment induces:

- Uniform downward band shift
- Energy bandgap narrowing

L.B. Ruppalt and J.W. Lyding, *Nanotechnology* **18**, 215202 (2007)

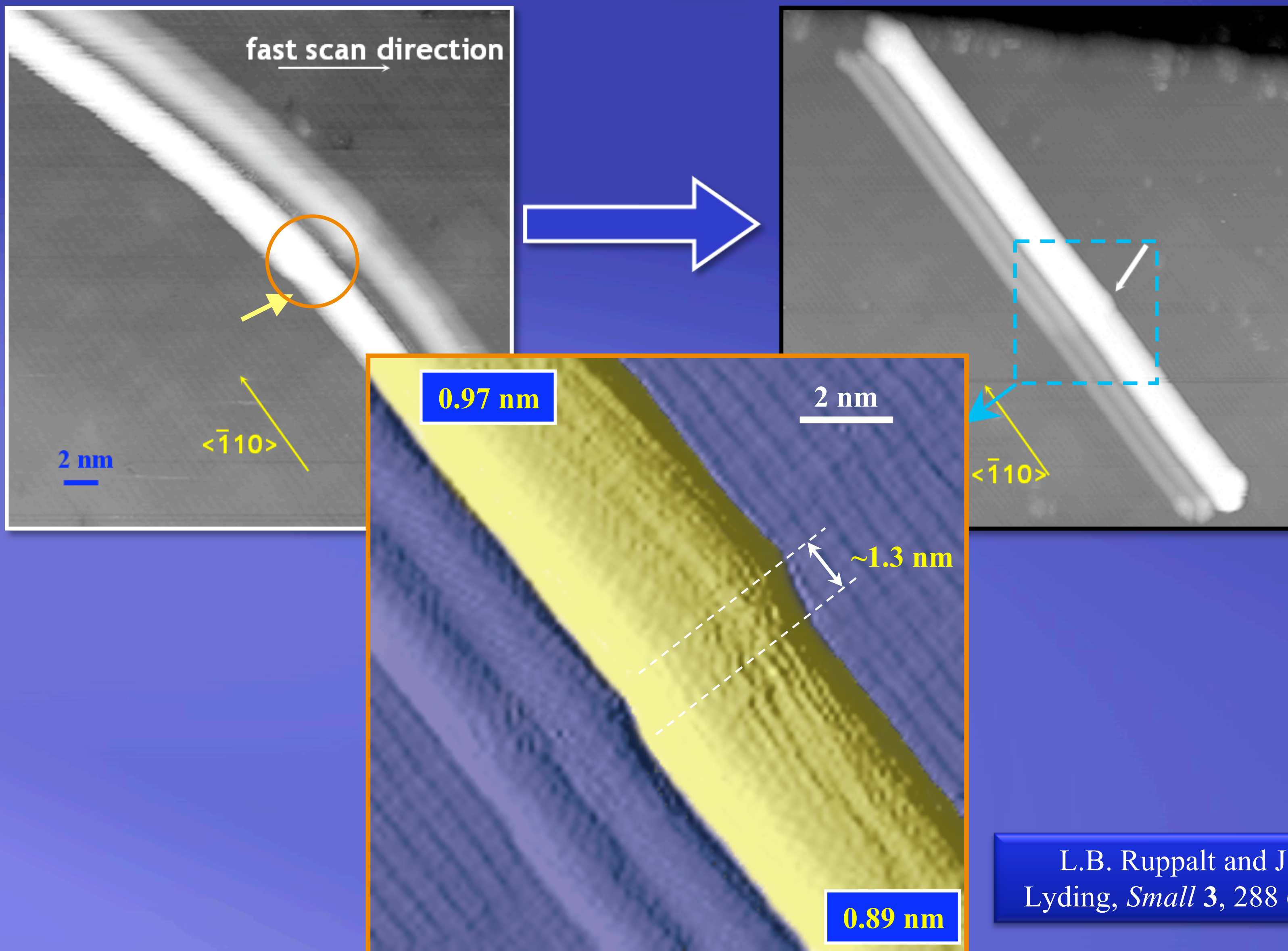
Nanotube Heterojunction on InAs(110)





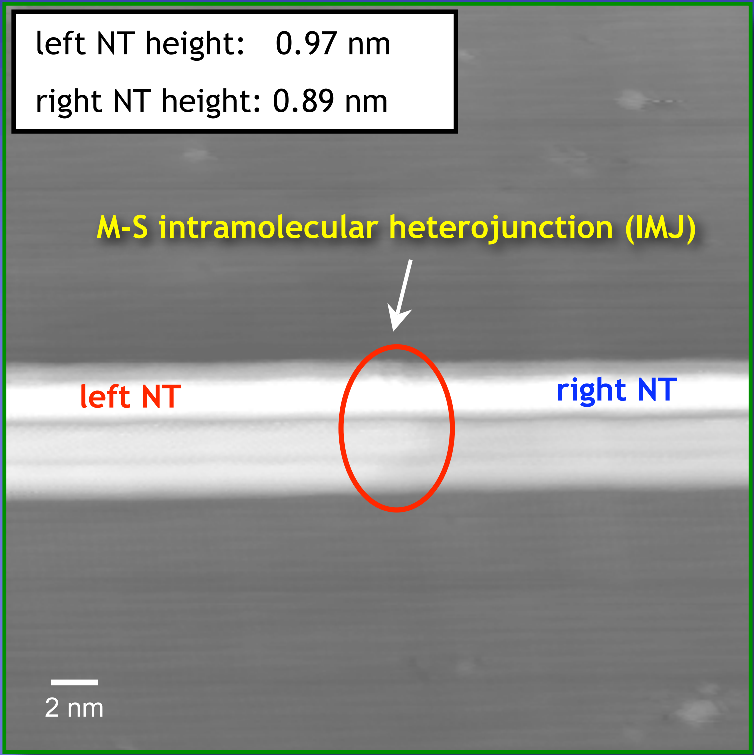
L.B. Ruppalt and J.W. Lyding, *Small* **3**, 288 (2007)

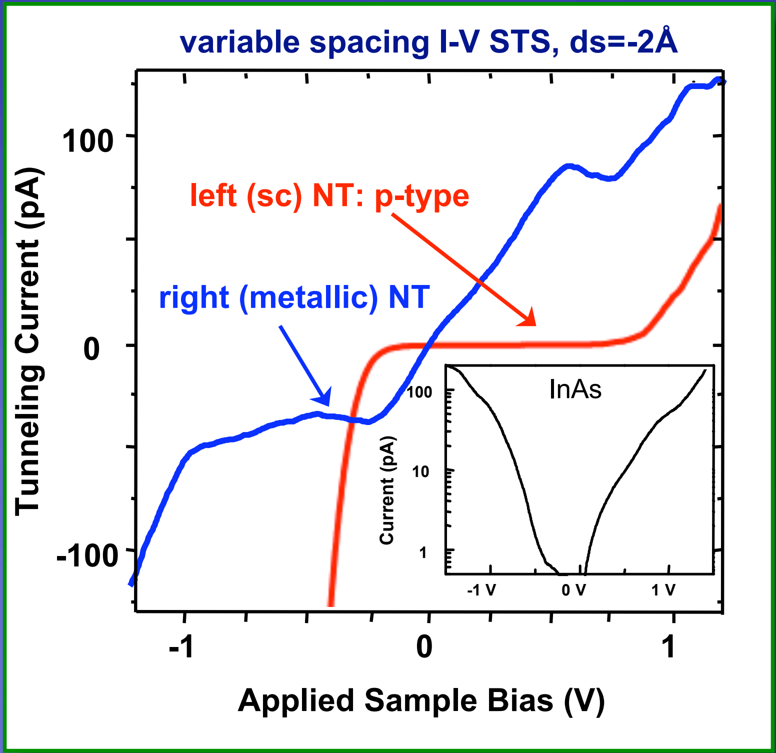
SWNT IMJ Identified via STM



L.B. Ruppalt and J.W. Lyding, *Small* **3**, 288 (2007)

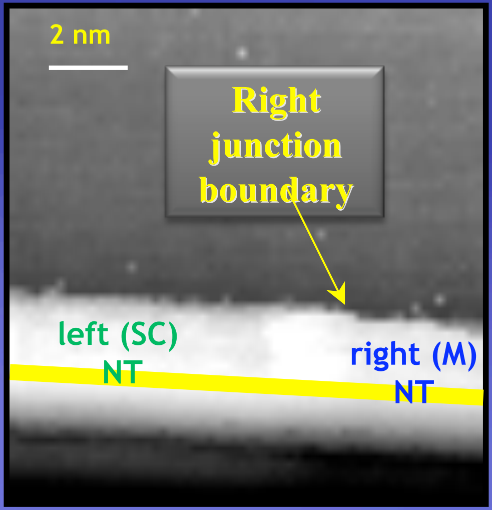
STM of intramolecular SWNT junction (IMJ)





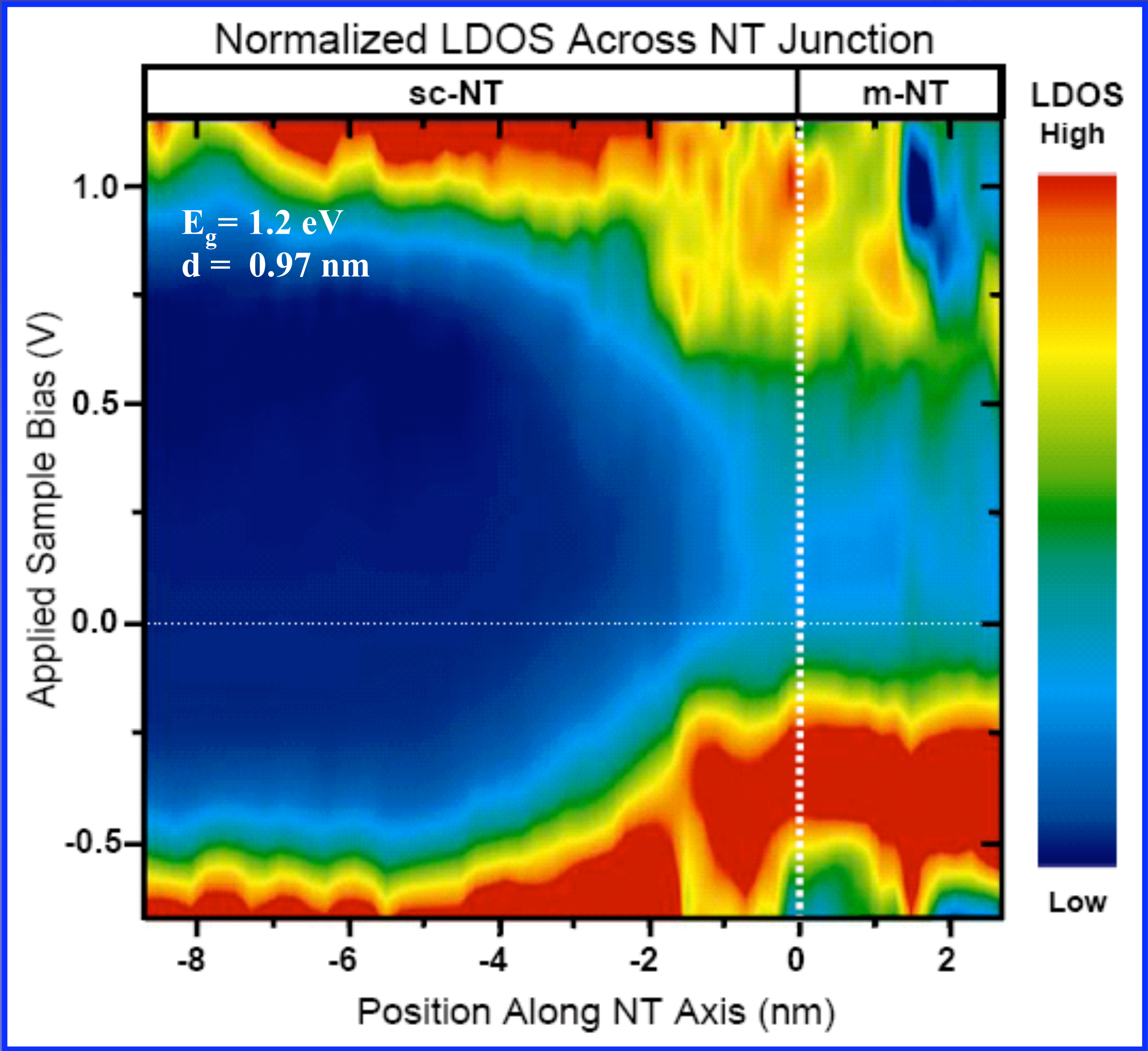
L.B. Ruppalt and J.W. Lyding, *Small* **3**, 288 (2007)

Spatially Resolved STS indicate MIGS at IMJ

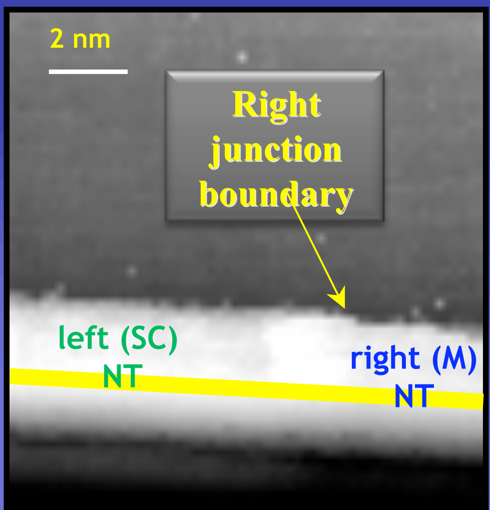


120 Å x 120 Å

Enhanced conductance in semiconducting nanotube (~3.7 nm) due to Metal Induced Gap States (MIGS)



Spatially Resolved STS indicate MIGS at IMJ



120 Å x 120 Å

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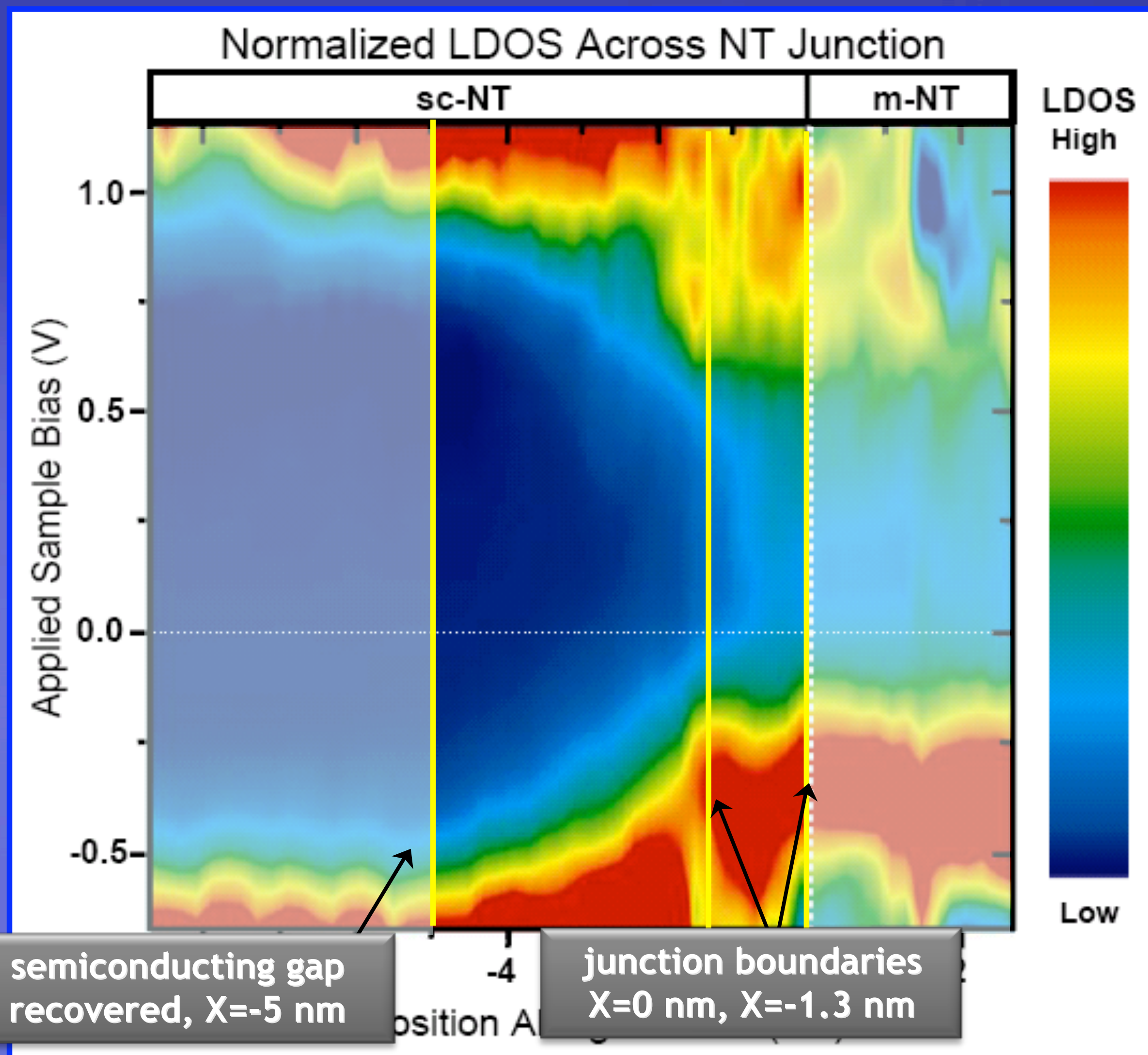
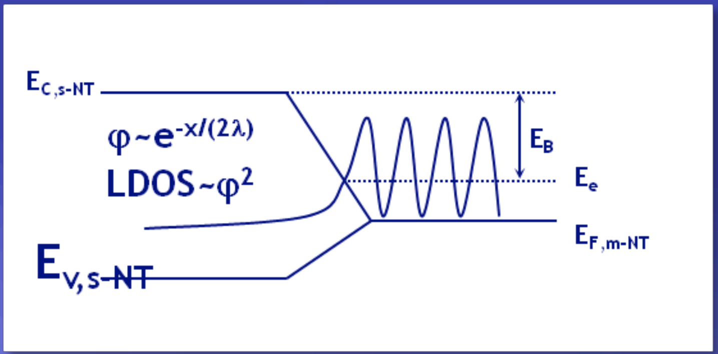
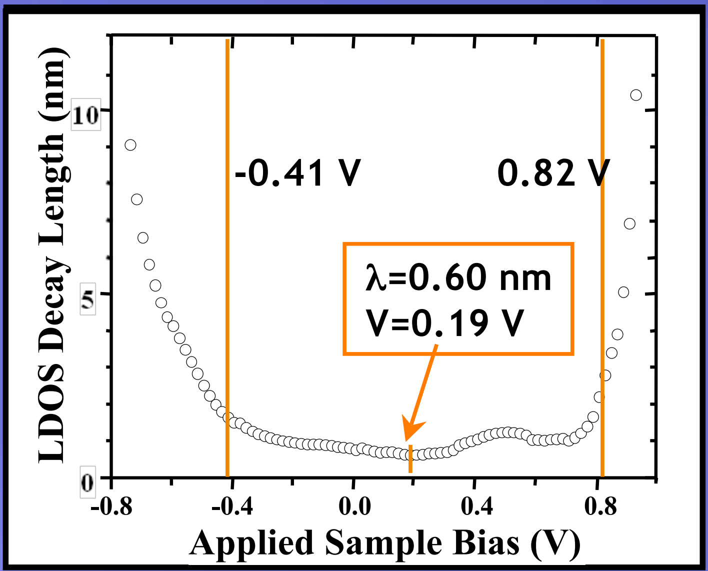
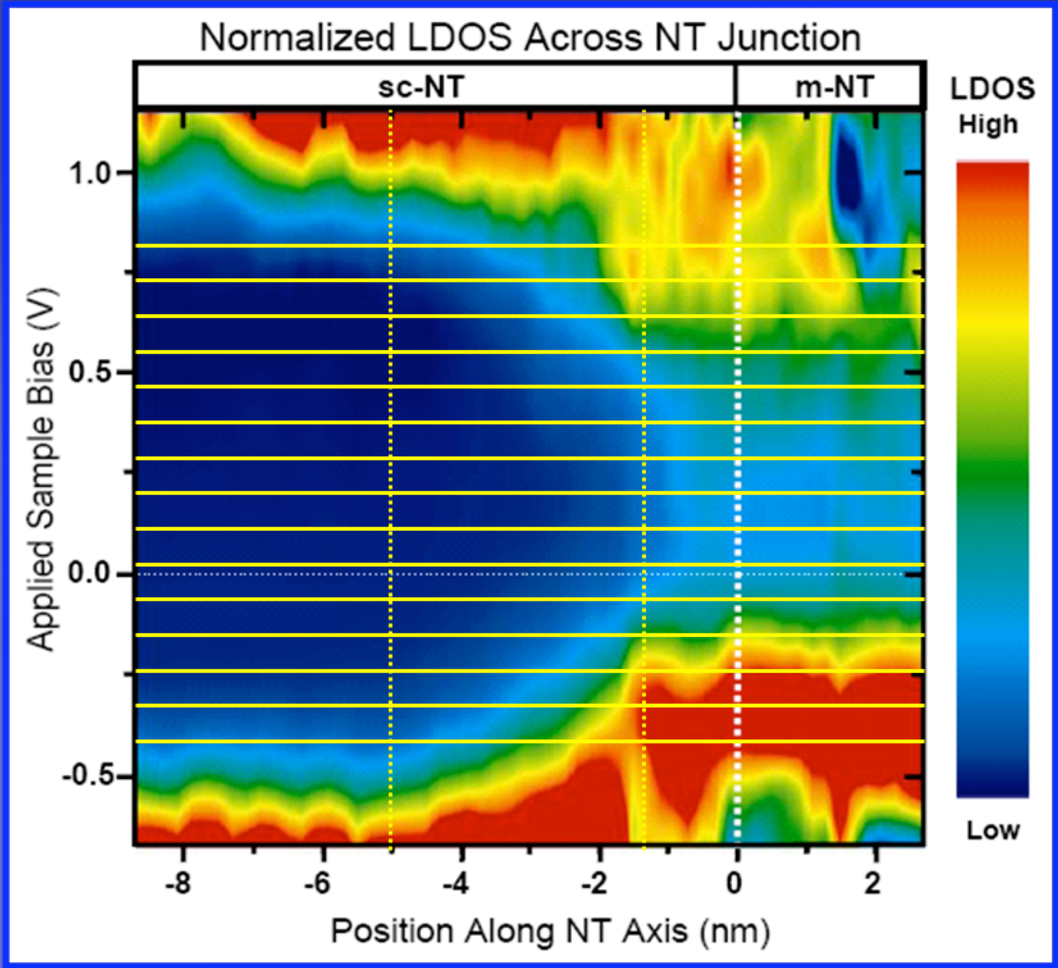


L.B. Ruppalt and J.W. Lyding, *Small* **3**, 288 (2007)

Spatially Resolved STS indicate MIGS at IMJ



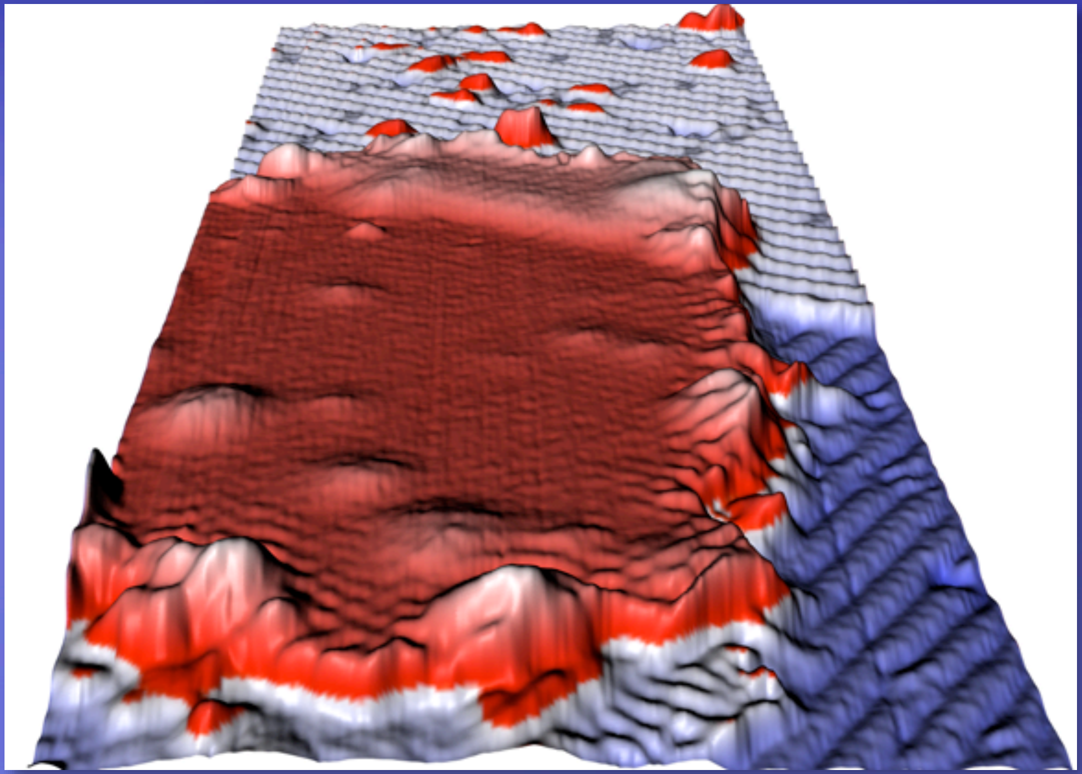




L.B. Ruppalt and J.W. Lyding, *Small* **3**, 288 (2007)

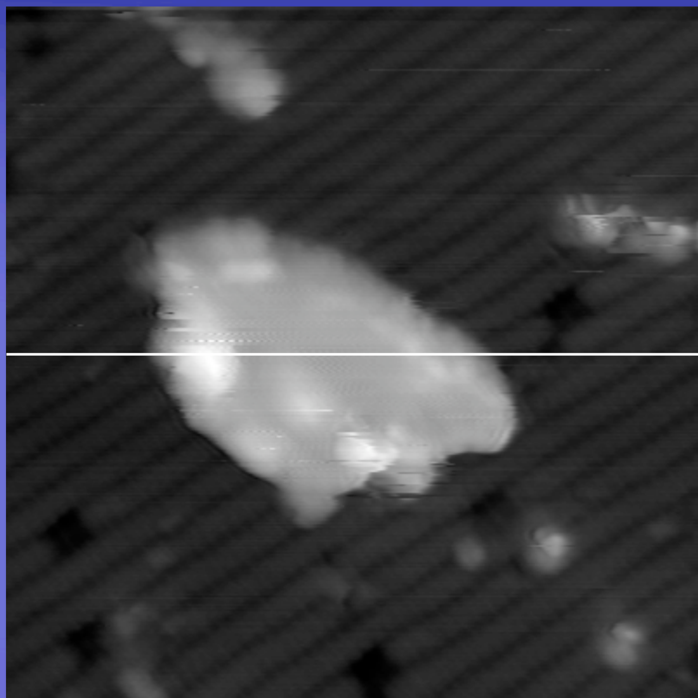
Graphene

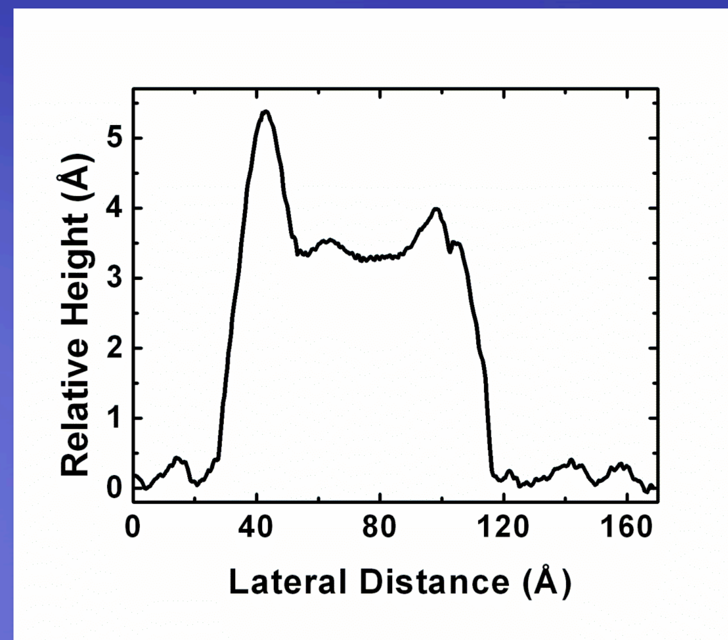
- Finite Size Effects
- Substrate Electronic Effects



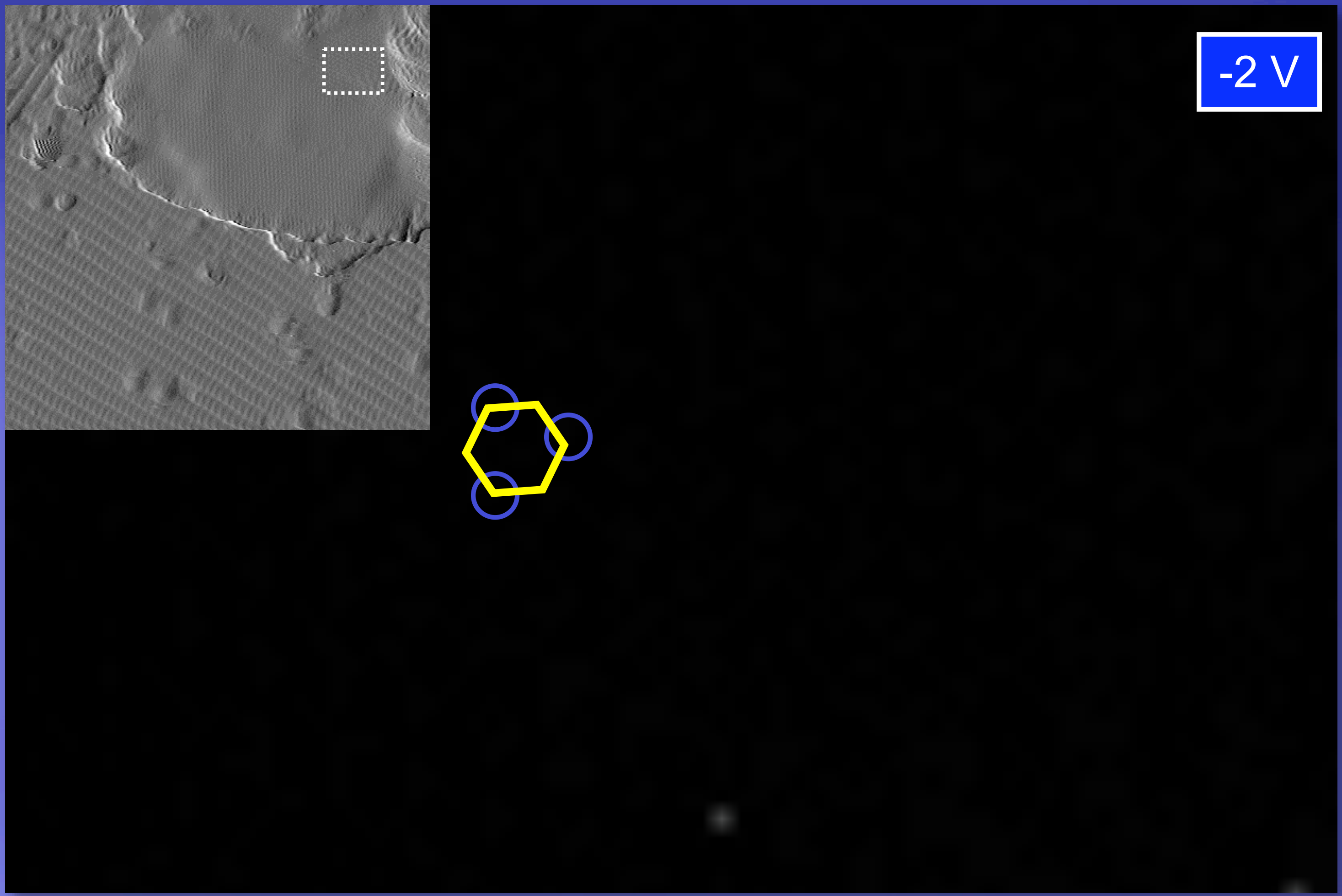
Kyle Ritter, Justin Koepke

Single Layer Graphene

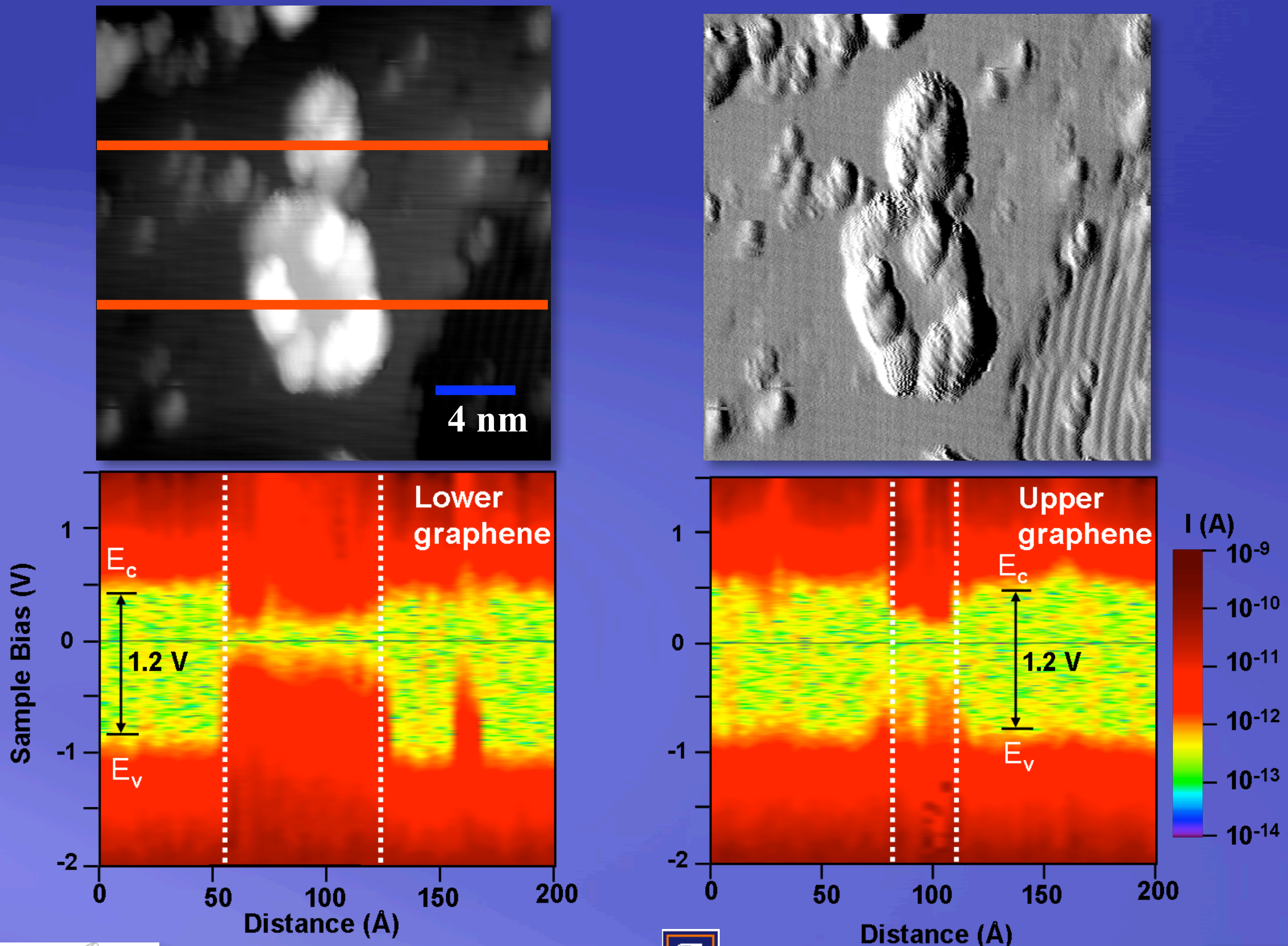




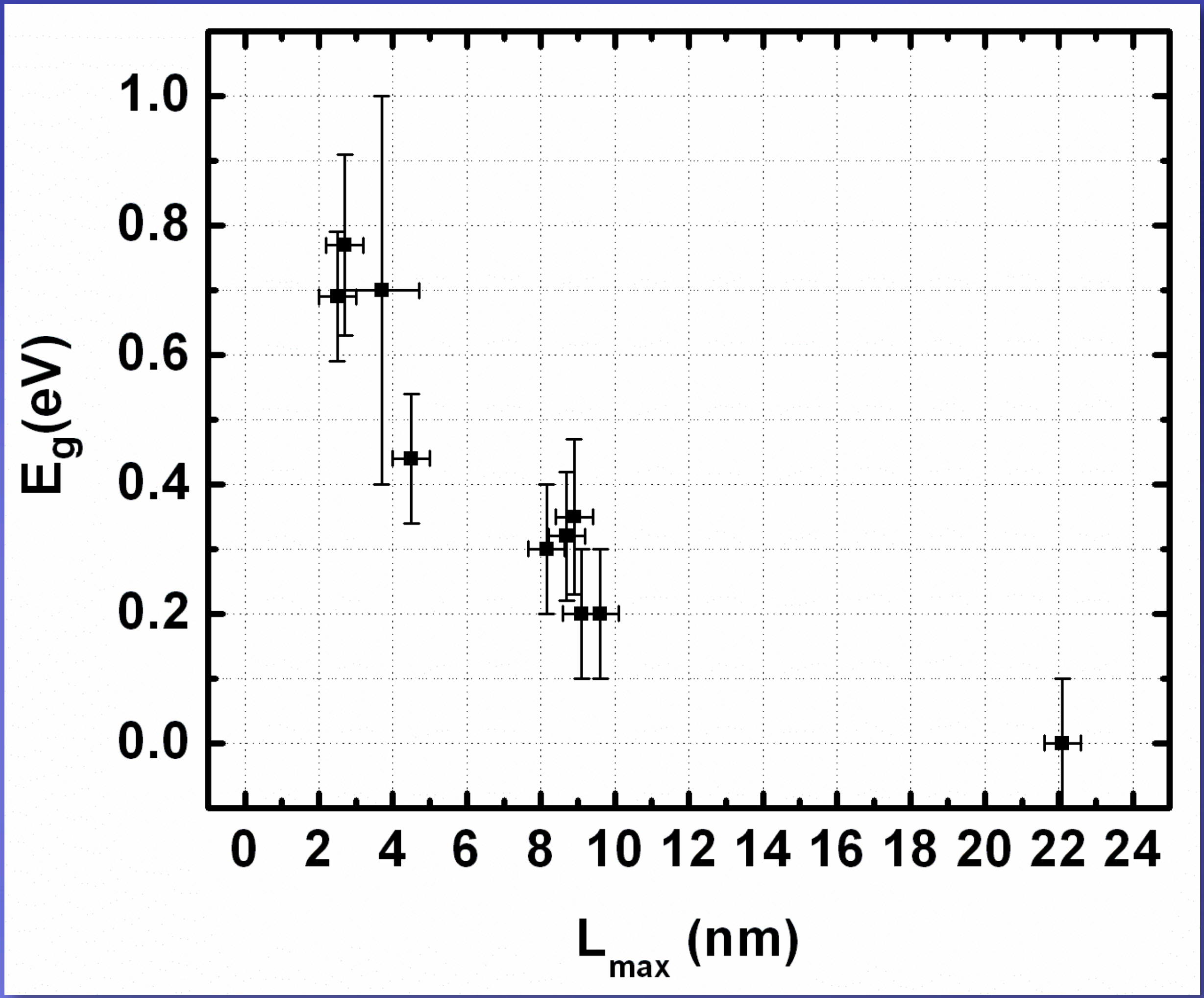
Double Layer Graphene



Graphene Spectroscopy: Finite Size Effect

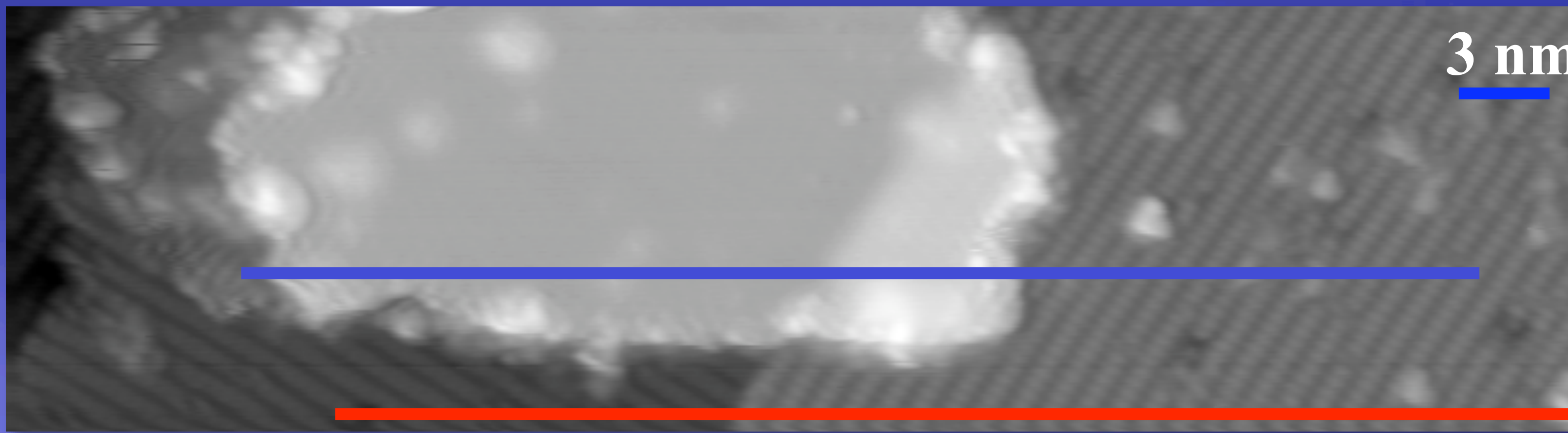


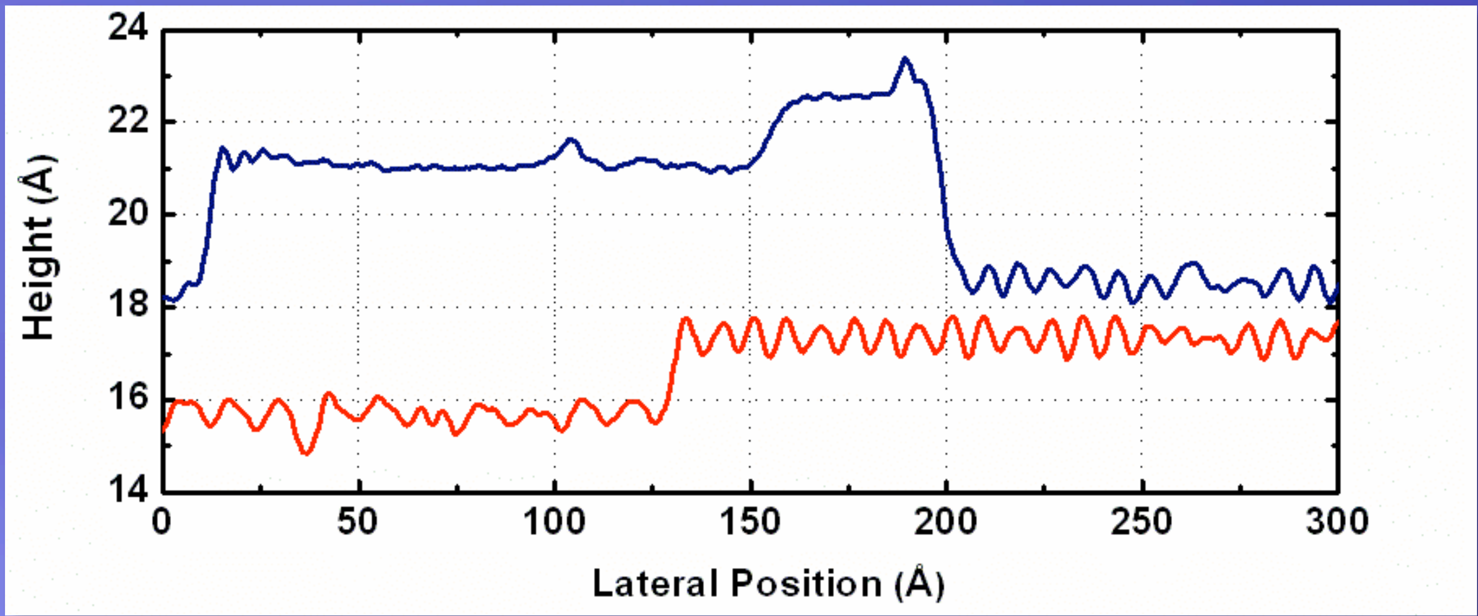
Graphene energy gap scales inversely with length



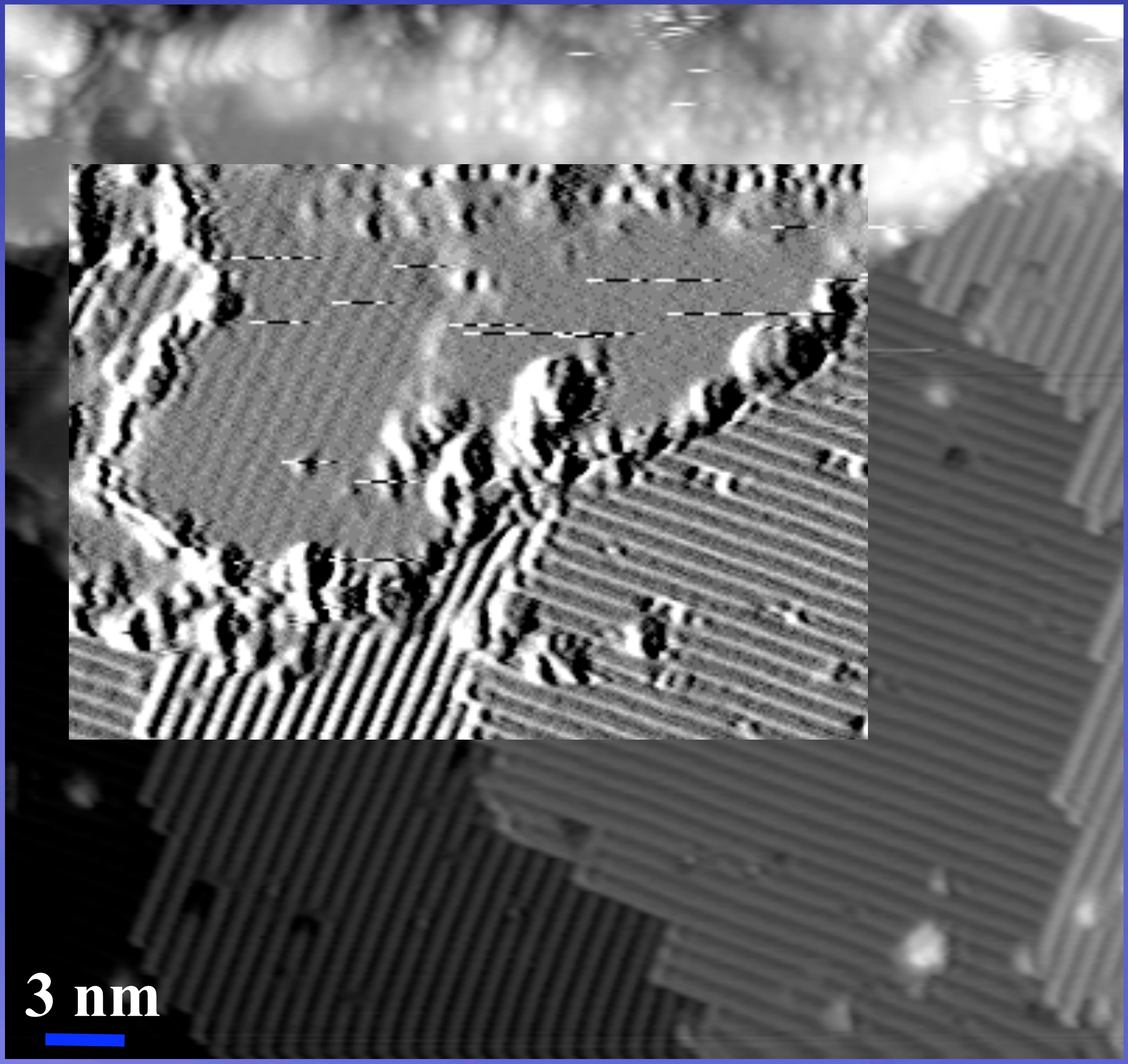
Kyle Ritter and Joe Lyding, Nanotechnology, in press.

Graphene: Substrate Effects



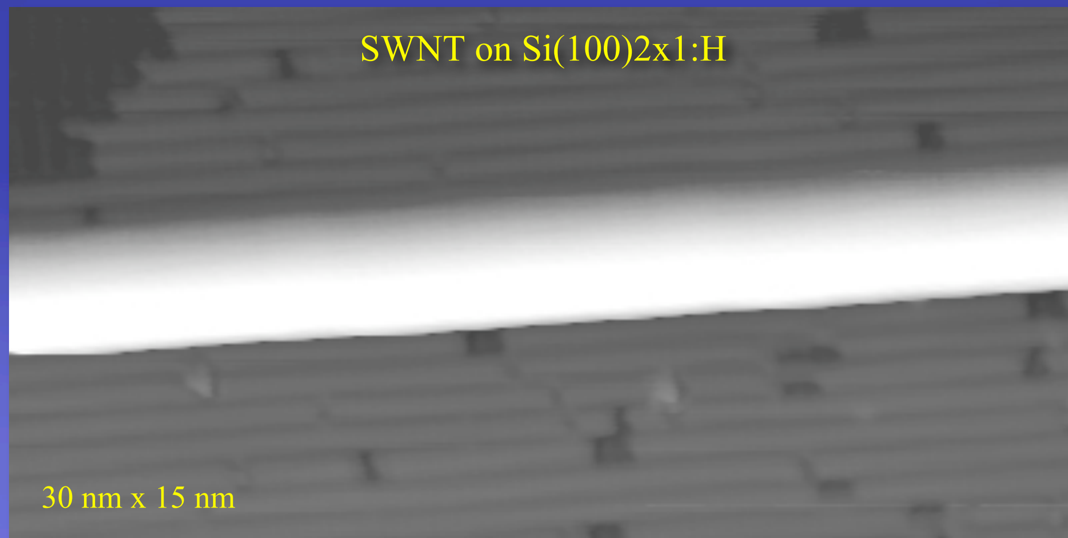


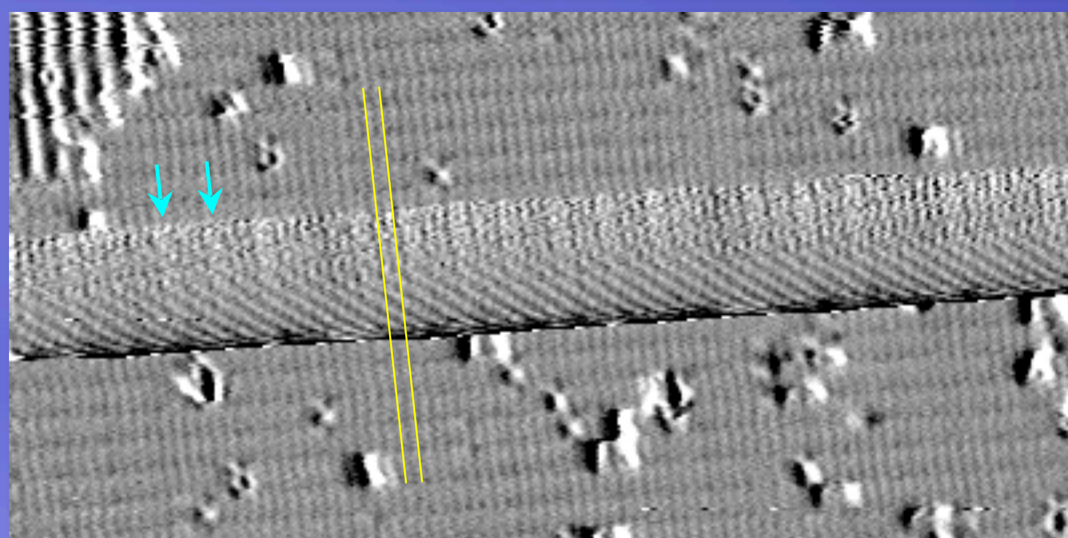
Graphene: Substrate Effects



Nanotube-Substrate Interaction

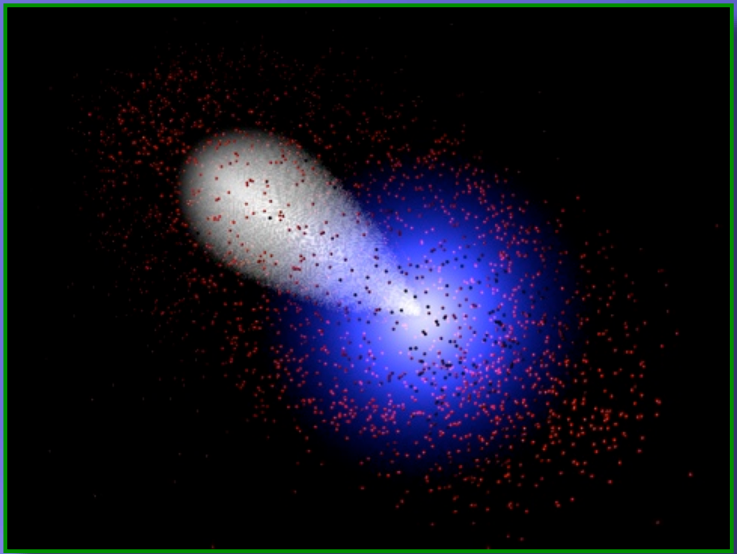
Substrate Structure Superimposed on Nanotube

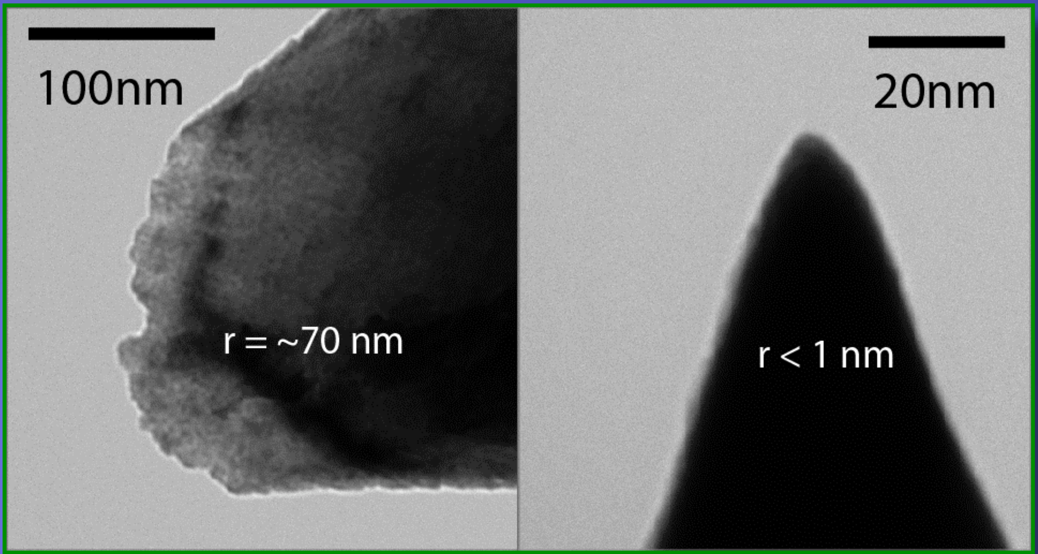




Ultra-Sharp (r < 1nm) STM Probes

- Field-Directed Sputter Sharpening (FDSS)
- Tungsten and Platinum-Iridium Probes
- STM Measurements

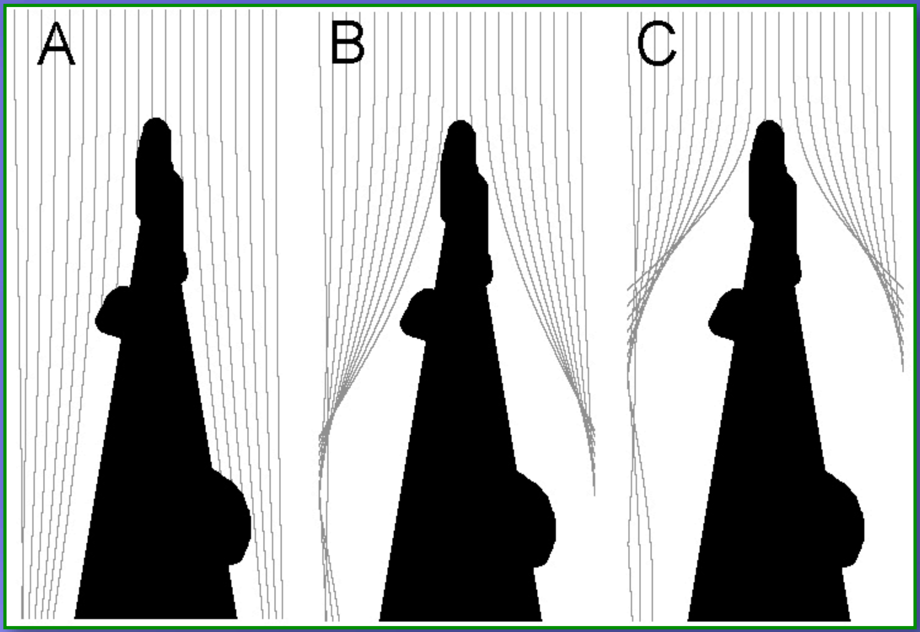


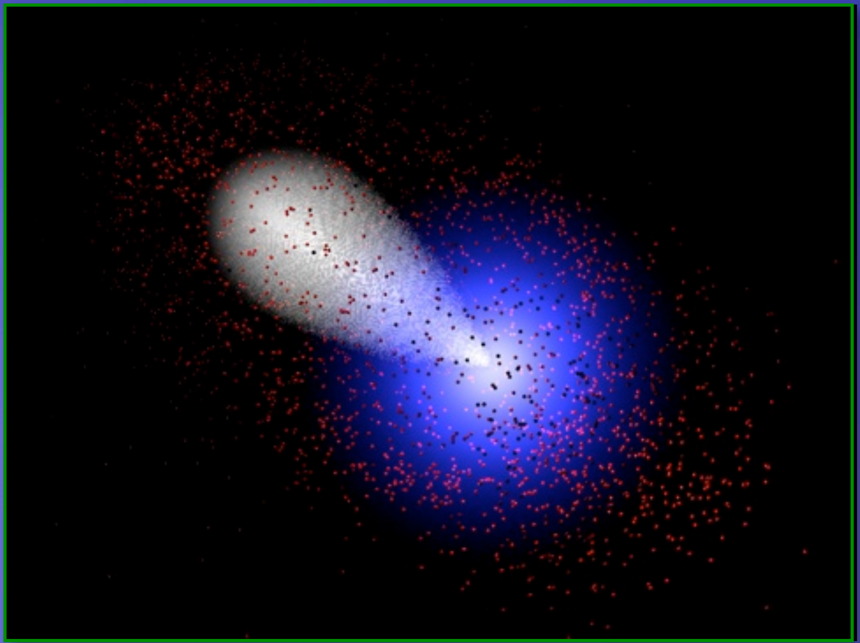


Scott Schmucker

Field-Directed Sputter Sharpening (FDSS)

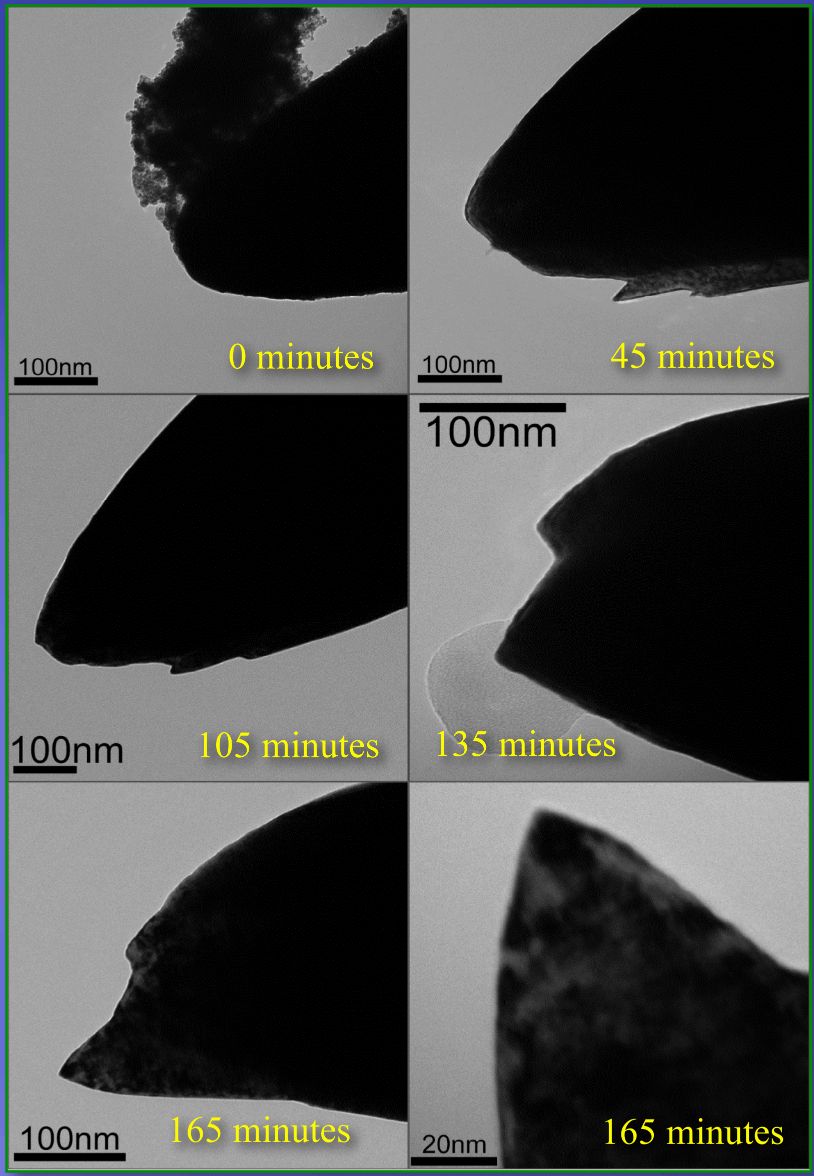
- Apply Positive Bias to Probe to Deflect Ions away from Apex
- Material Surrounding Apex is Preferentially Sputtered – Sharpening Apex
- Sharpened Apex Enhances Field-Directed Process, ultimately leading to Self-Limited Sharpness (r < 1 nm)



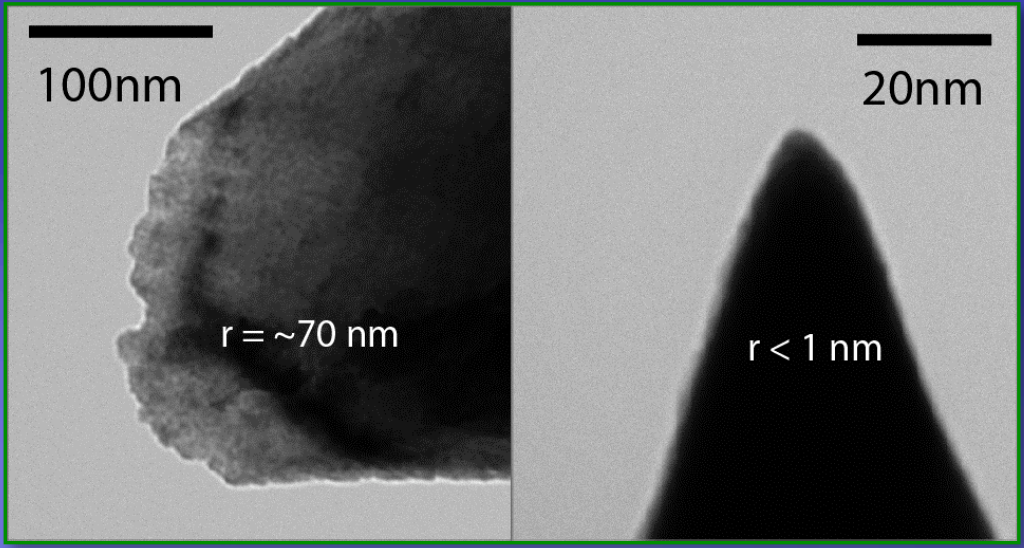


Note: FDSS is compatible with batch processing.

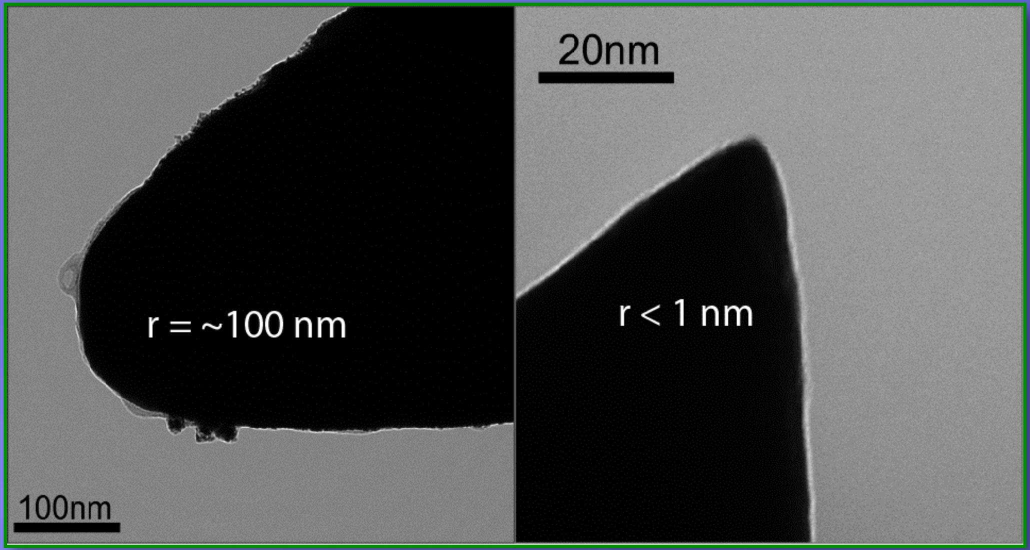
PtIr Probe: Incremental Sharpening



Sharpening: TEM Imaging

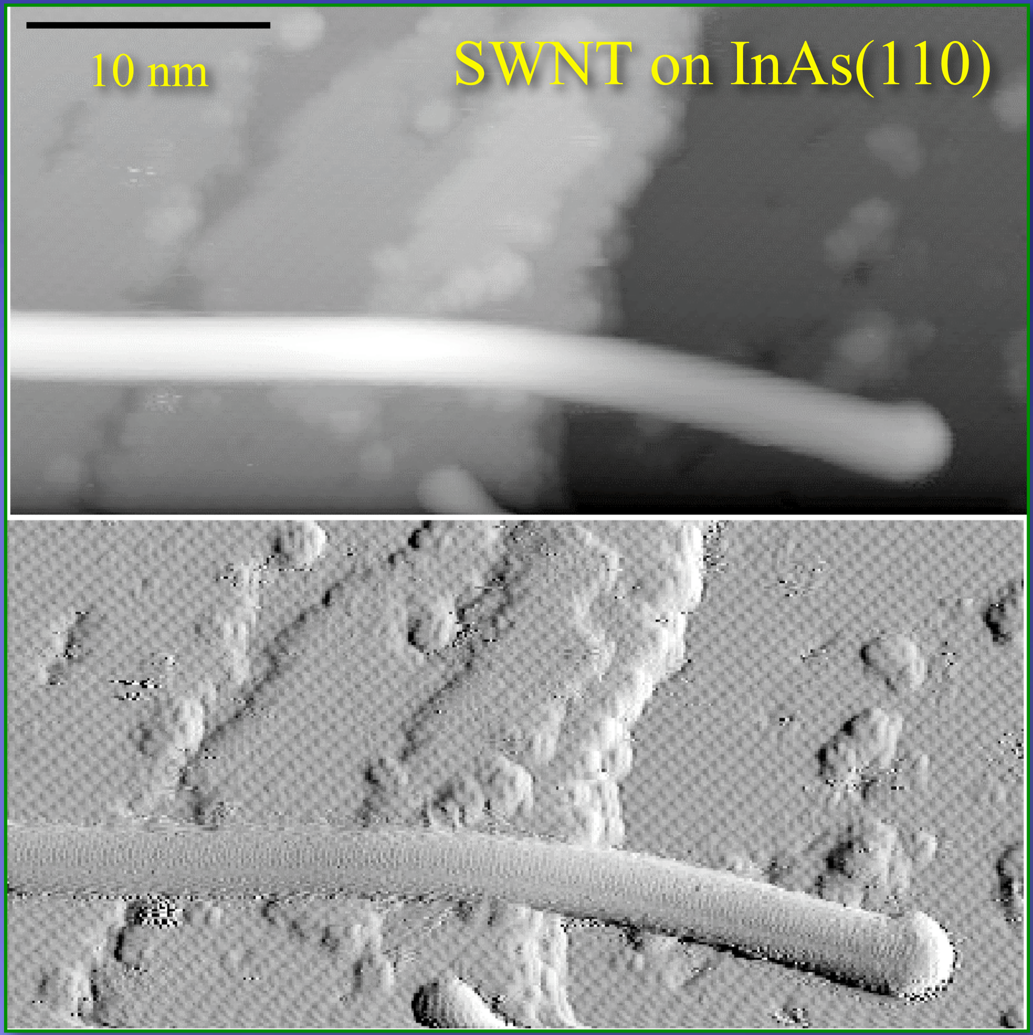


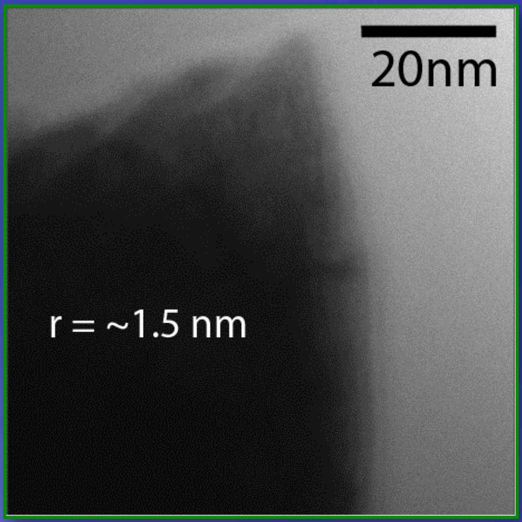
Polycrystalline Tungsten
Tip Bias: +200 V
1.2 keV Neon Ions
62 minutes



Platinum-Iridium
Tip Bias: +400 V
2.0 keV Neon Ions
35 minutes

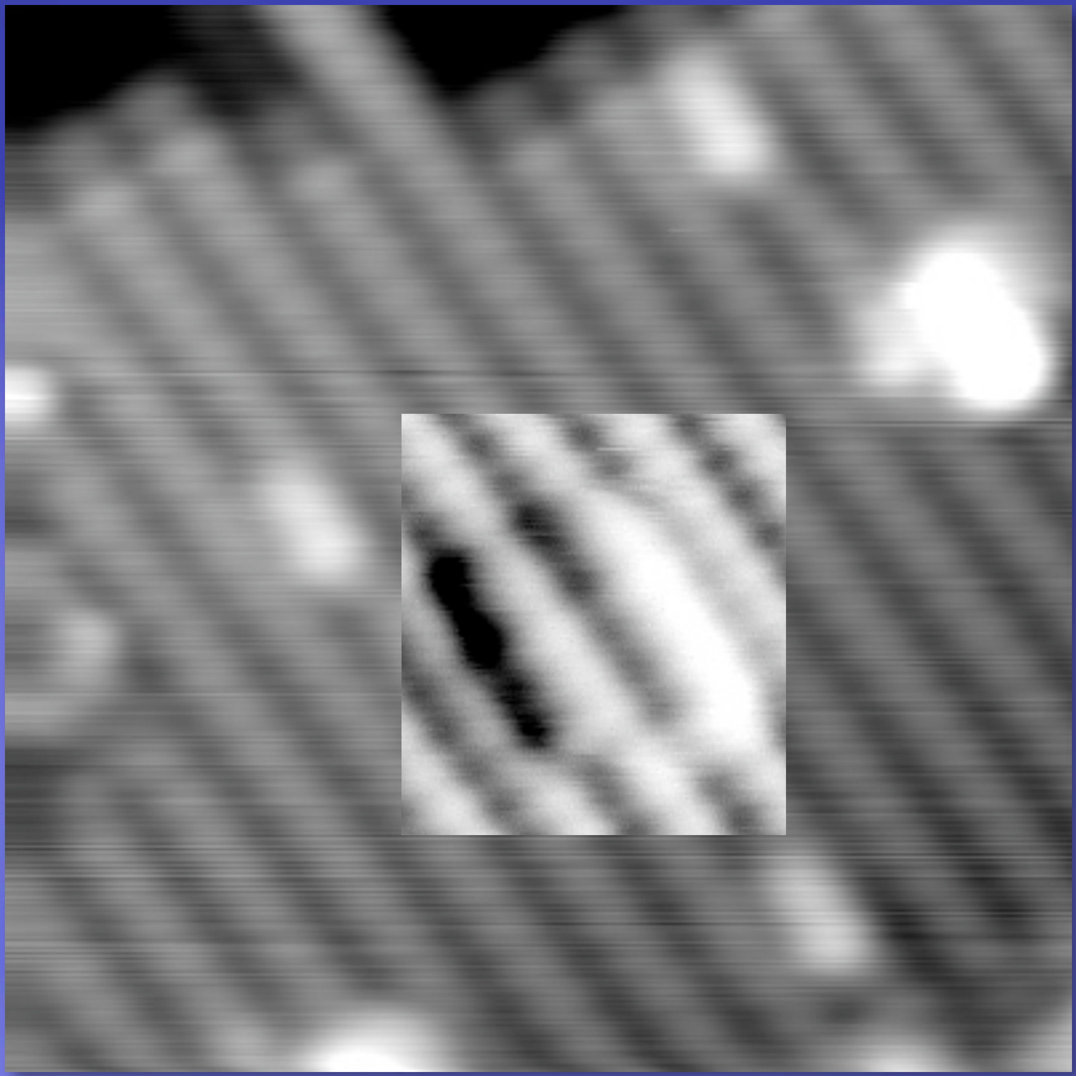
STM Imaging



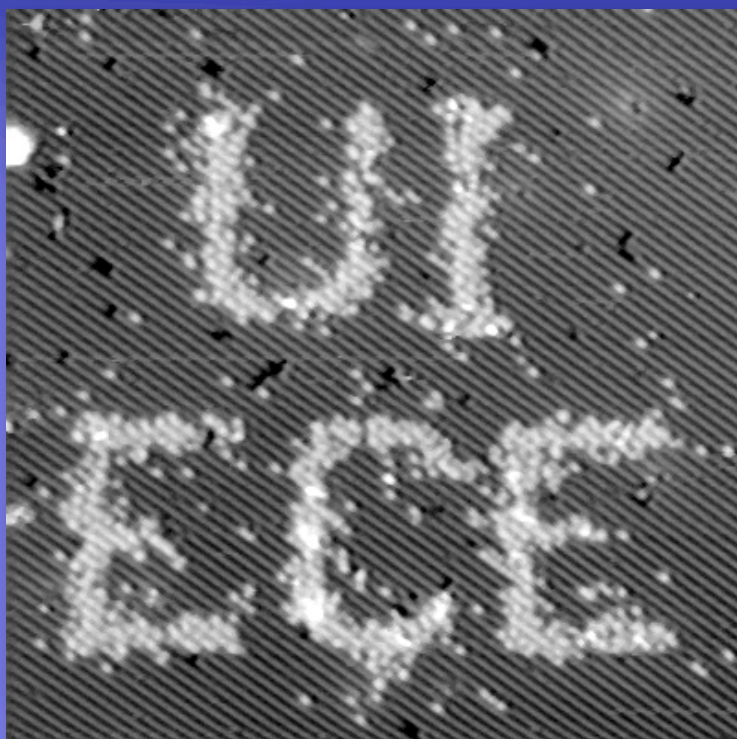


Poly-Tungsten
Tip Bias: +400 V
2.0 keV Neon Ions
35 minutes

STM Patterning



In conclusion…



•The DCT technique enables the ultra-clean fabrication of carbon nanotubes and graphene on clean semiconductor surfaces.

•Atomic scale STM and STS elucidates the detailed nature of the nanostructure-substrate interaction.

Acknowledgements

UIUC STM Group

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Greg Scott
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Wei Ye

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Intel

NSF

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