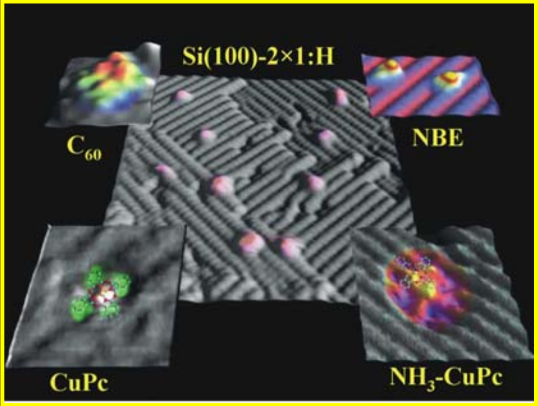
Atomic-Scale Nanoelectronics



Mark C. Hersam
Assistant Professor

Department of Materials Science and Engineering,
Northwestern University, Evanston, IL 60208-3108
Ph: 847-491-2696, m-hersam@northwestern.edu
WWW: http://pubweb.northwestern.edu/~mhe663/

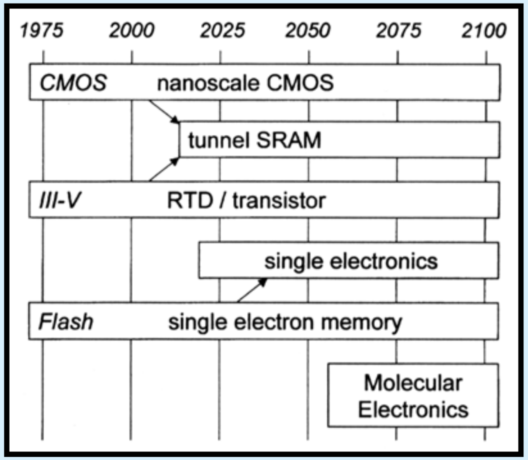
IEEE ED/CAS/SSC
Chicago Chapter Meeting

October 25, 2001
Schaumburg, Illinois

Molecular Nanoelectronics on Silicon?

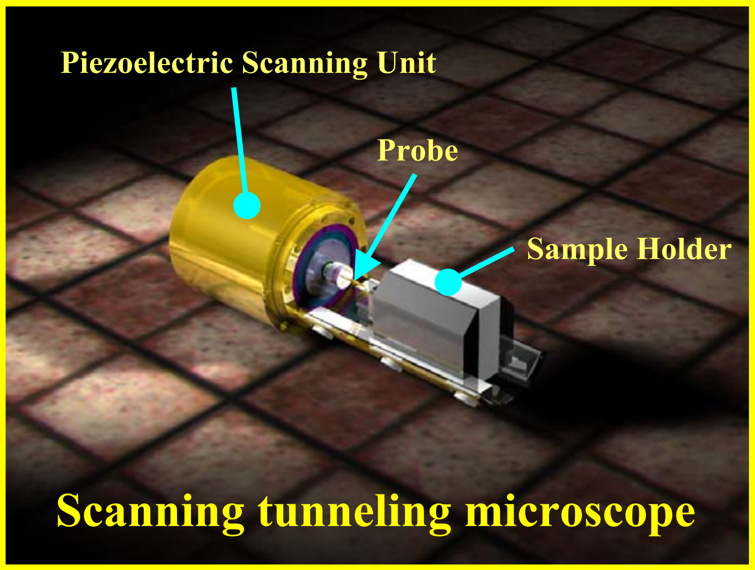
<u>Projected timeline for the electronics industry</u>:

A. C. Seabaugh, P. Mazumder,
Proceedings of the IEEE, <u>87</u>, 535 (1999).



What can we do today?

Outline



Study silicon-based molecular nano-technology issues with the UHV-STM

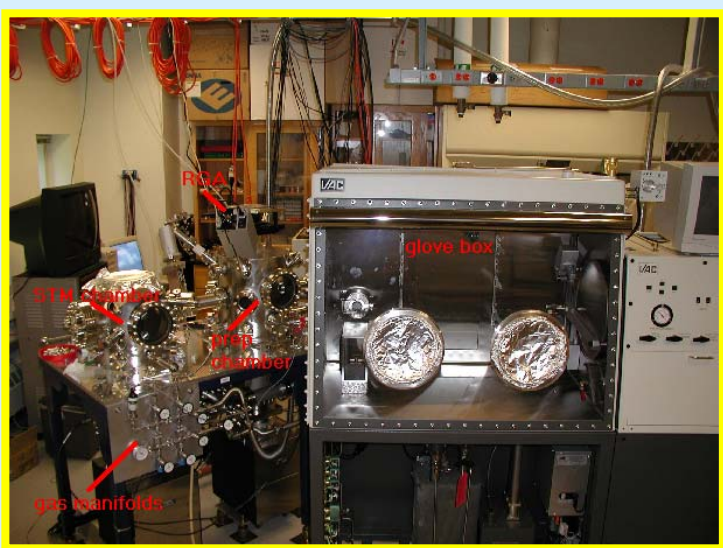
- **Bottom-up approach in a pristine environment**
- **Studies on silicon bridge the gap between fundamental research and modern technology**

Outline:

(1) Robustness of Si(100)-2×1:H surface
(2) STM-induced desorption: Implications for nanofab and CMOS
(3) FCL: Single molecule studies (Organic and biological molecules)
(4) Hybrid nanoelectronics and conventional microelectronics

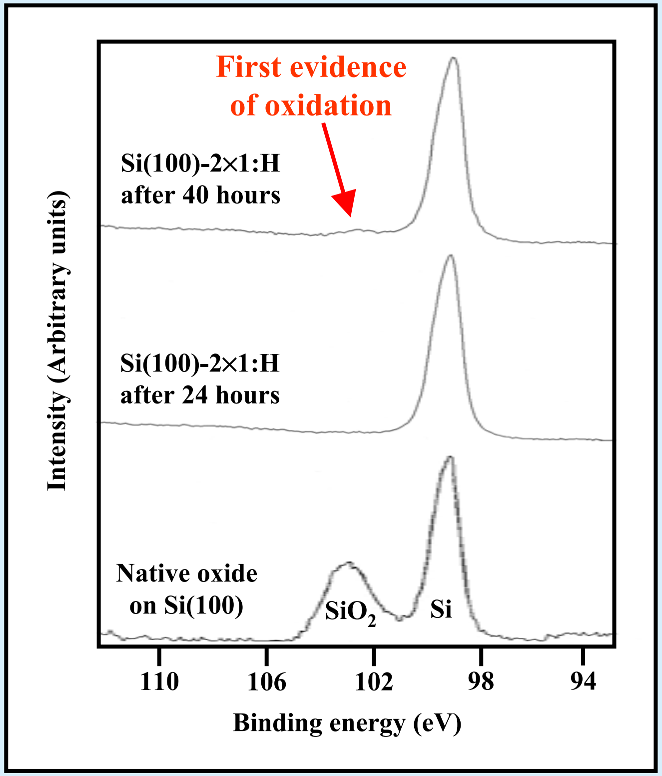
Equipment / Facilities

- ThermoMicroscopes CP Research ® atomic force microscope (AFM)
- Room temperature ultra-high vacuum (UHV) scanning tunneling microscope (STM) interfaced to controlled atmosphere glove box
- Cryogenic UHV STM with variable temperature control between 10 K and 400 K.

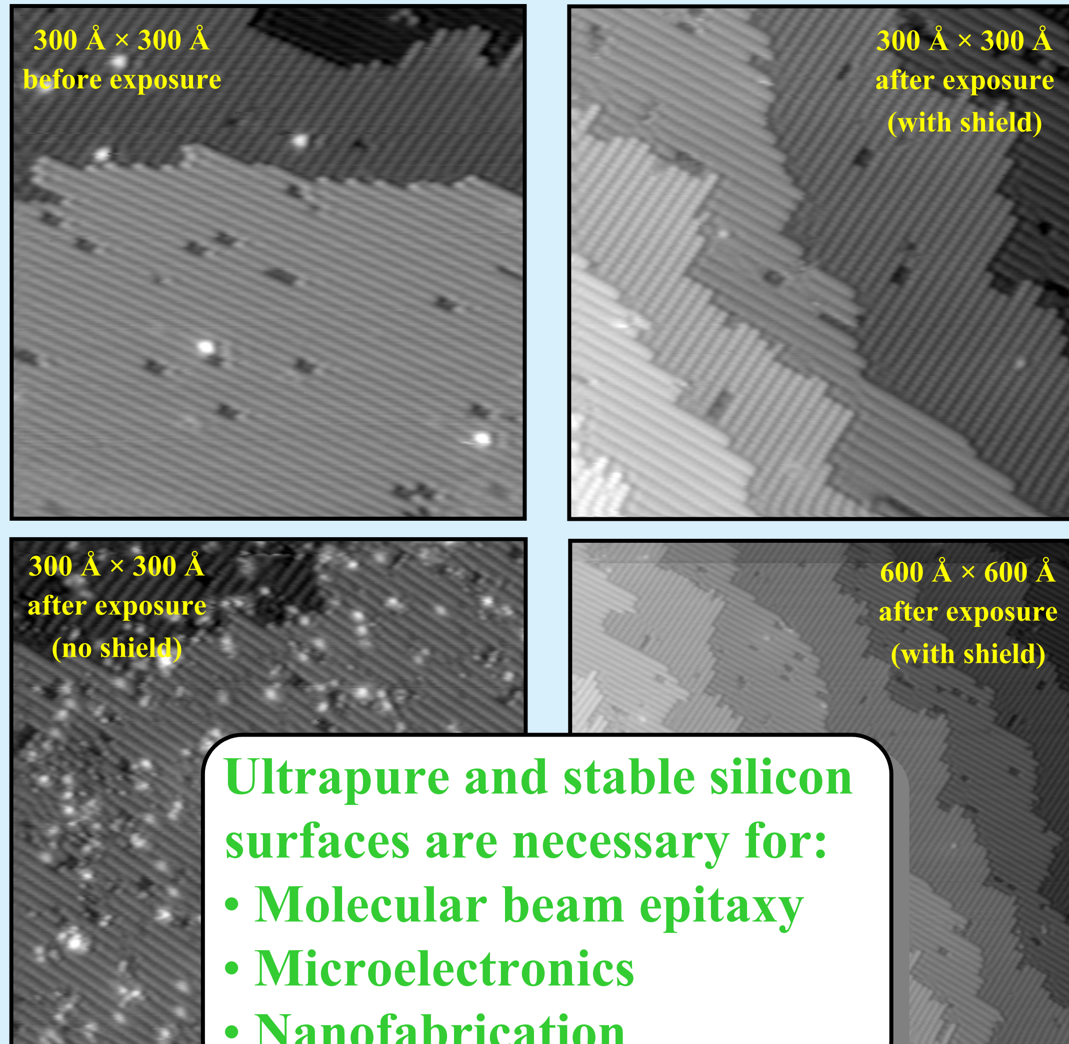


Robustness of Si(100)-2×1:H

M. C. Hersam, D. S. Thompson, N. P. Guisinger, J. S. Moore, and J. W. Lyding, *Appl. Phys. Lett.*, 78, 886 (2001).



XPS results after ambient exposure

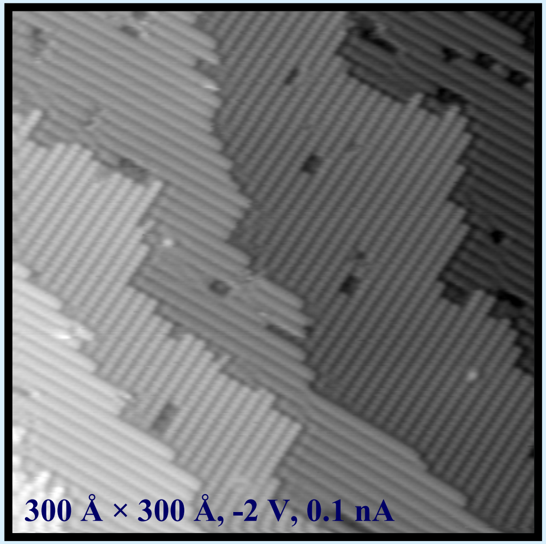


Ultrapure and stable silicon surfaces are necessary for:

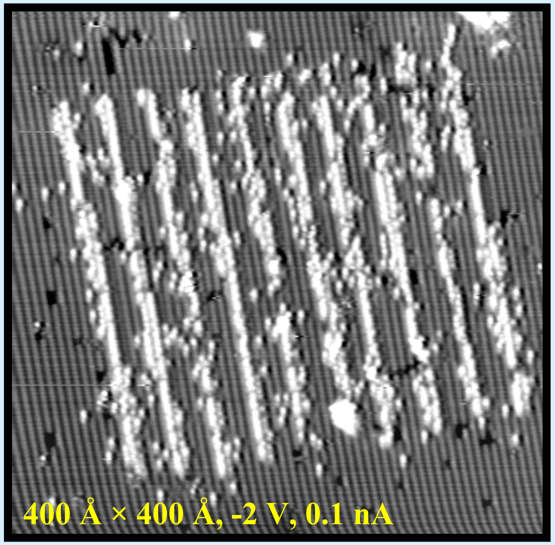
- Molecular beam epitaxy
- Microelectronics
- Nanofabrication

Nanolithography on H Passivated Si(100)

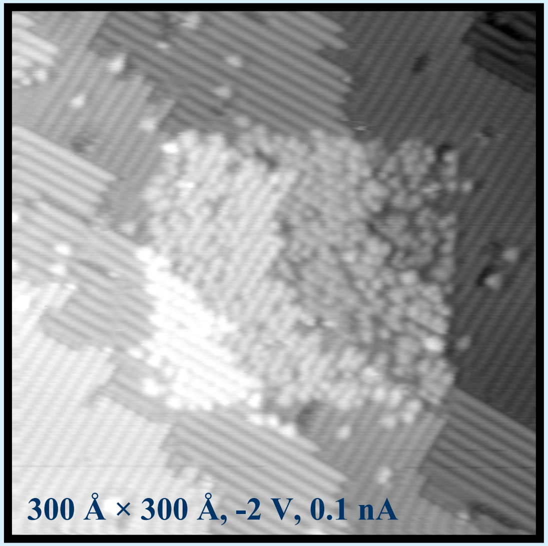
J. W. Lyding, T.-C. Shen, J. S. Hubacek, J. R. Tucker, and G. C. Abeln, *Appl. Phys. Lett.*, 64, 2010 (1994).



A relatively stable and unreactive surface is produced by hydrogen passivating the Si(100)-2×1 surface in ultra-high vacuum (UHV).



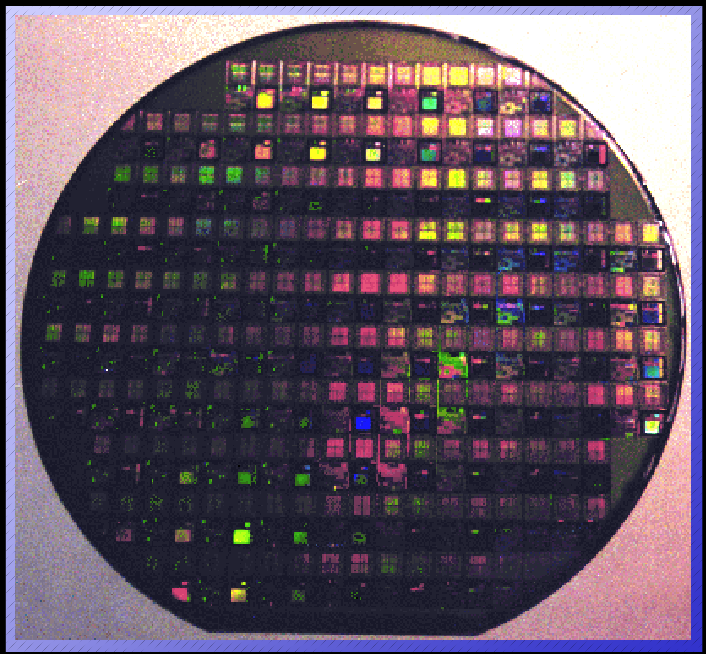
Highly reactive "dangling bonds" are created by using the STM as a highly localized electron beam.



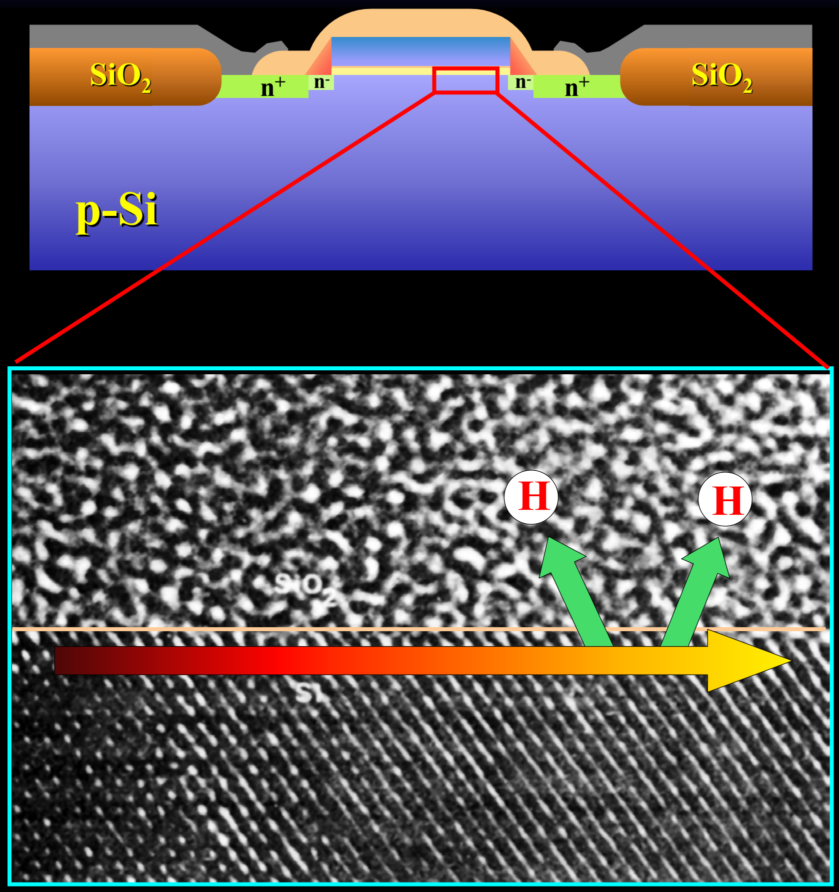
The linewidth and desorption yield are a function of the incident electron energy, the current density, and the total electron dose.

- Selective chemistry can be accomplished on patterned areas.
- Large isotope effect exists between hydrogen and deuterium.

CMOS ⟷ STM Analogy

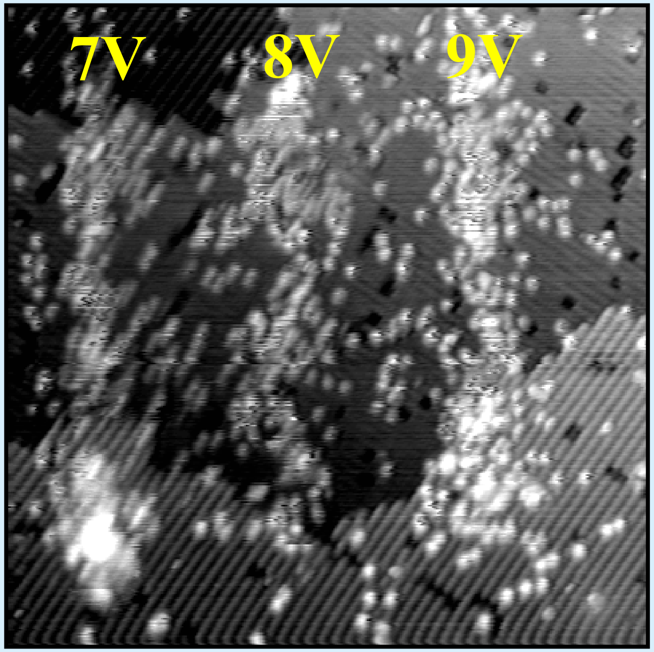


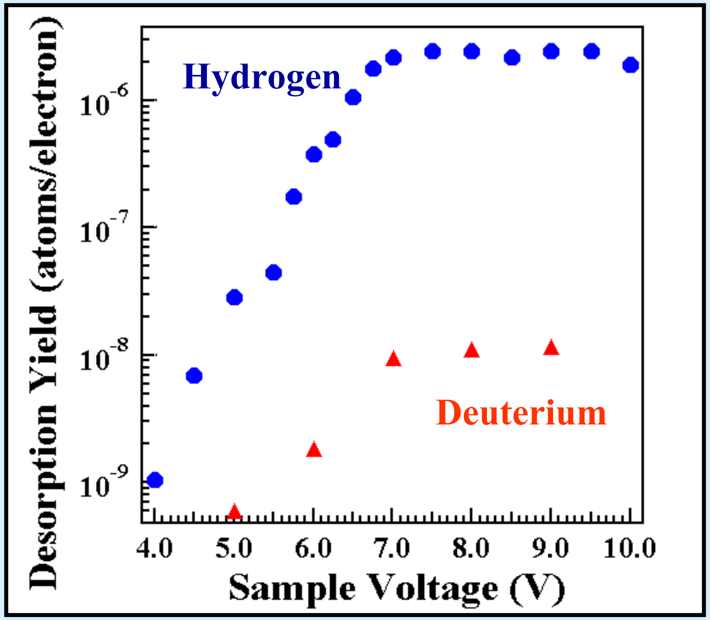
Conventional Silicon Microelectronics



Electron Stimulated Desorption Isotope Effect

Ph. Avouris, R. E. Walkup, A. R. Rossi, T.-C. Shen, G. C. Abeln, J. R. Tucker, and J. W. Lyding, *Chem. Phys. Lett.*, 257, 148 (1996).

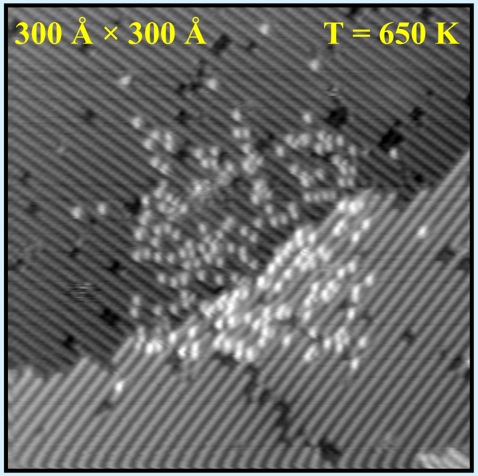


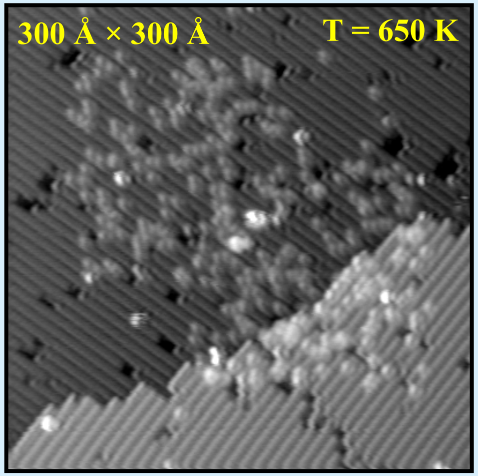


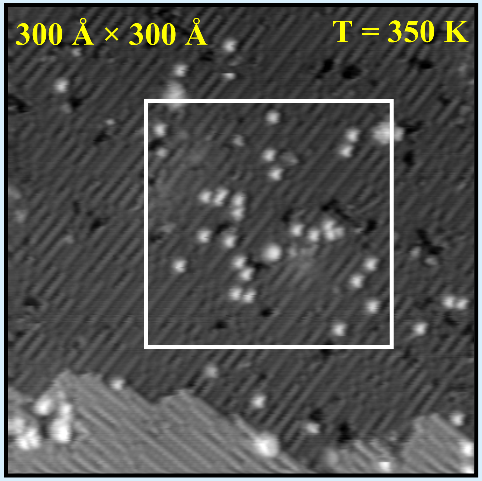
- Deuterium has a much lower ESD yield than hydrogen.
- Desorption conditions exist where all of the hydrogen and none of the deuterium is removed from the surface.
- Deuterating CMOS devices leads to longer device lifetimes.

Direct Measurement of D:H Ratio

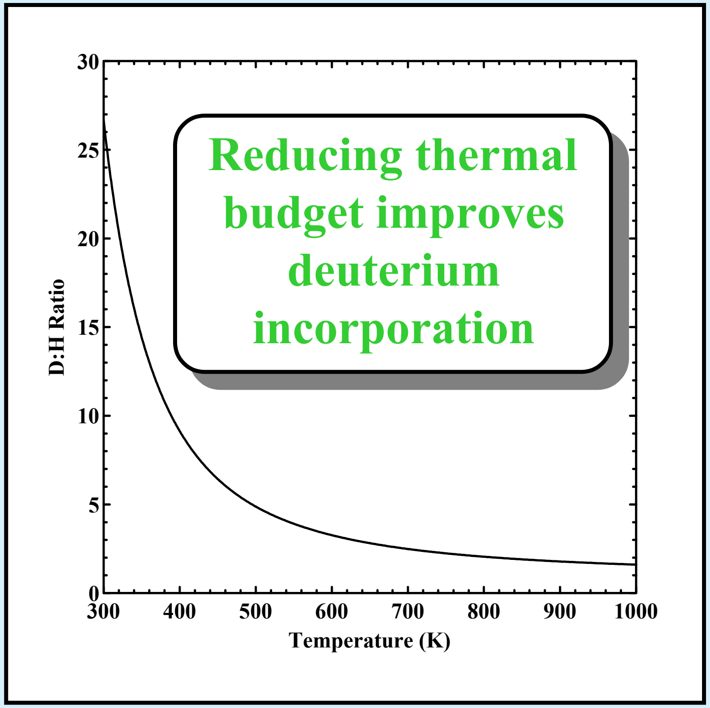
M. C. Hersam, K. Cheng, N. P. Guisinger, J. Lee, and J. W. Lyding, submitted to *Appl. Phys. Lett.* (2001).







Passivation at 650 K ⇒ D:H Ratio ~ 5
Passivation at 350 K ⇒ D:H Ratio ~ 50



Statistical thermodynamics model confirms experimental results.

Department of Materials Science and Engineering, Northwestern University

Silicon-Based Molecular Nanoelectronics

Goal: Single Molecule Electronic Switching and Storage

Conformational or Electronic State Transitions

Approach: Bottom-Up UHV STM -> Atomic Resolution

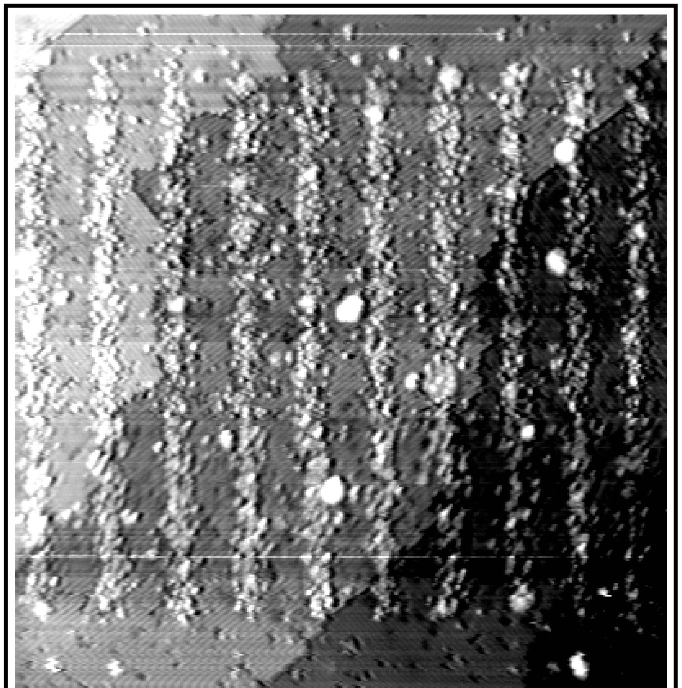
- Hydrogen Resist Technique, Selective Molecular Adsorption
- Feedback Controlled Lithography
- Single Molecule Studies (NBE, CuPc & C_{60})
- Nanoscale Contacting Scheme

New Directions

New Molecules, Nanobioelectronics, Nanochemical Analysis

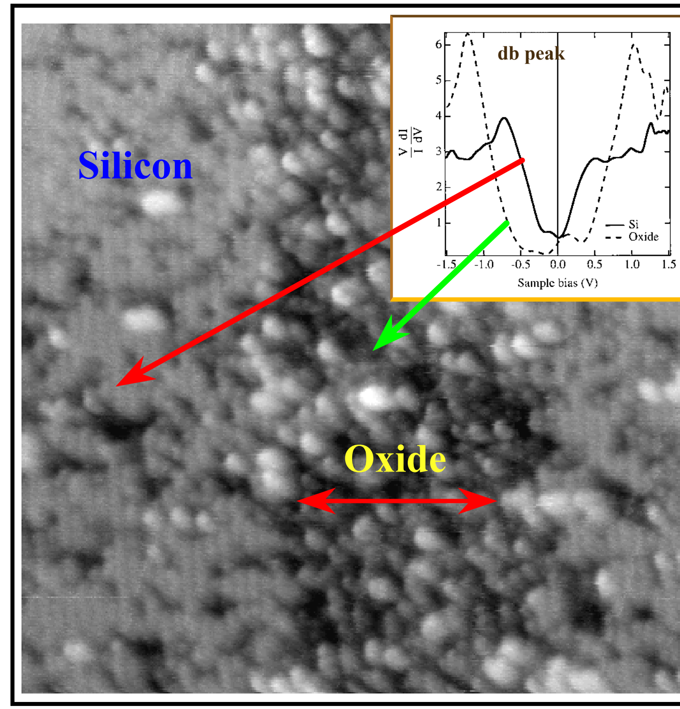
Selective Oxidation

UHV Oxidation @ 10^{-6} Torr



J. W. Lyding, T.-C. Shen, J. S. Hubacek, J. R. Tucker, and G. C. Abeln, *Appl. Phys. Lett.*, 64, 2010 (1994).

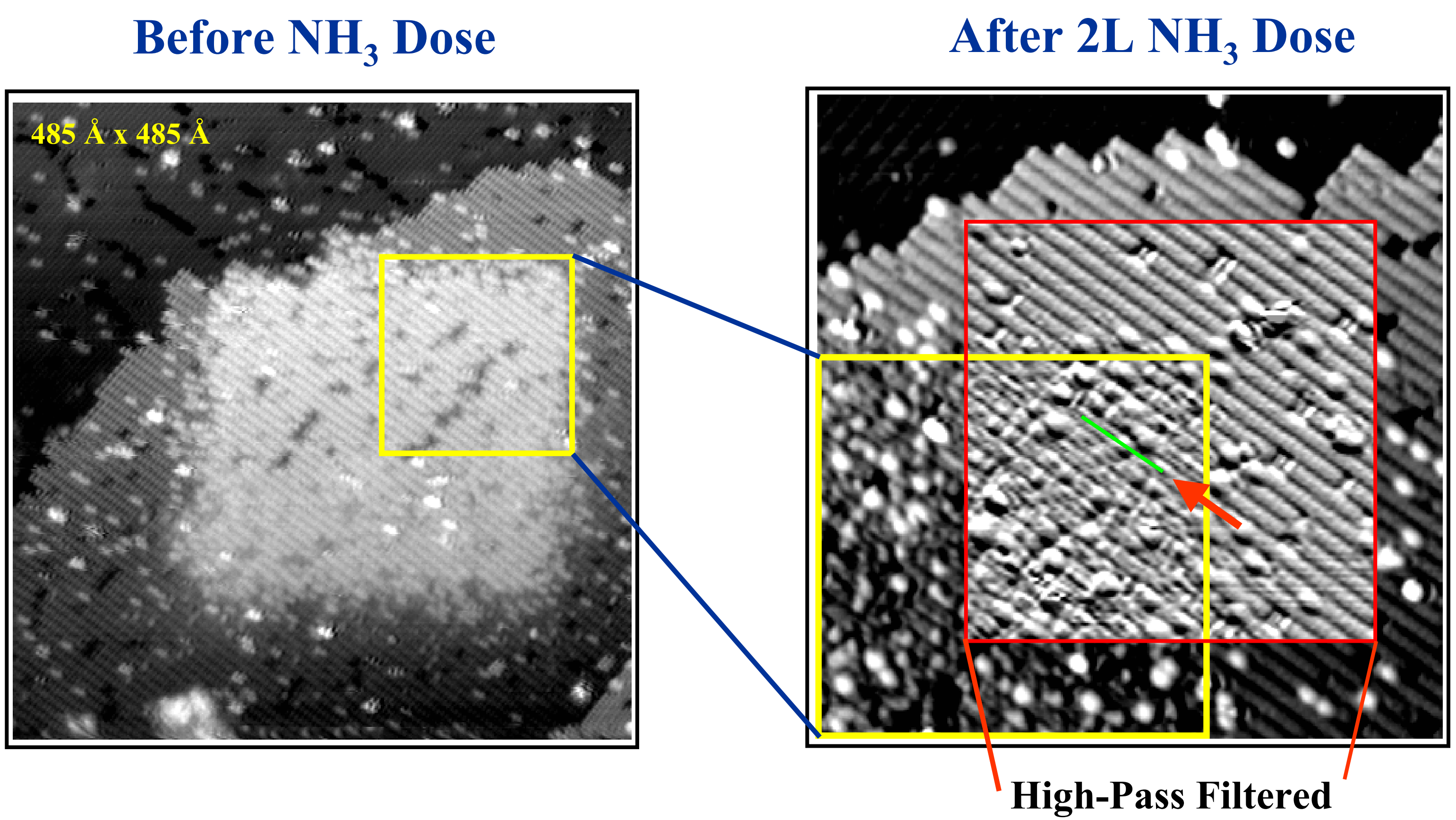
Loadlock Oxidation @ 4 psi



T.-C. Shen, C. Wang, J. W. Lyding, and J. R. Tucker, *Appl. Phys. Lett.*, 66, 976 (1995).

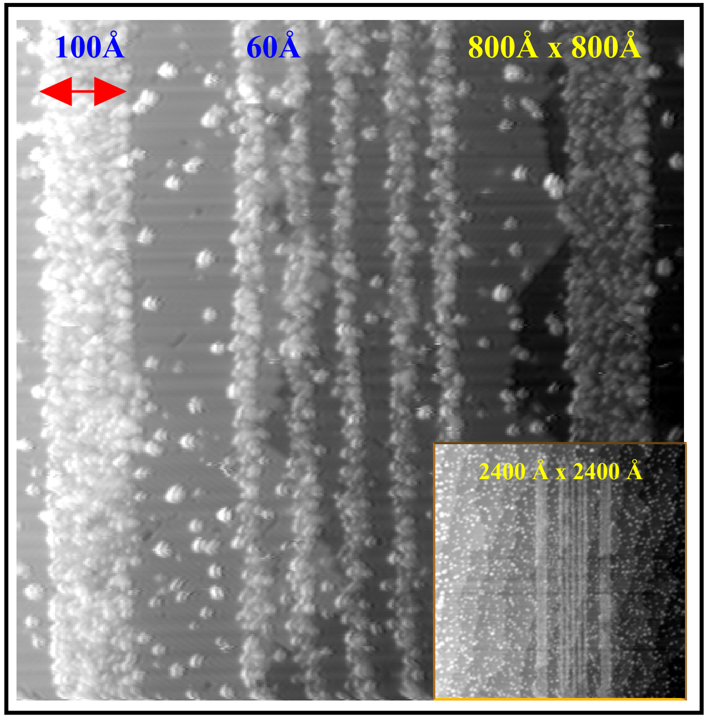
Selective Nitridation

J. W. Lyding, T.-C. Shen, G. C. Abeln, C. Wang, and J. R. Tucker, *Nanotechnology*, 7, 128 (1996).



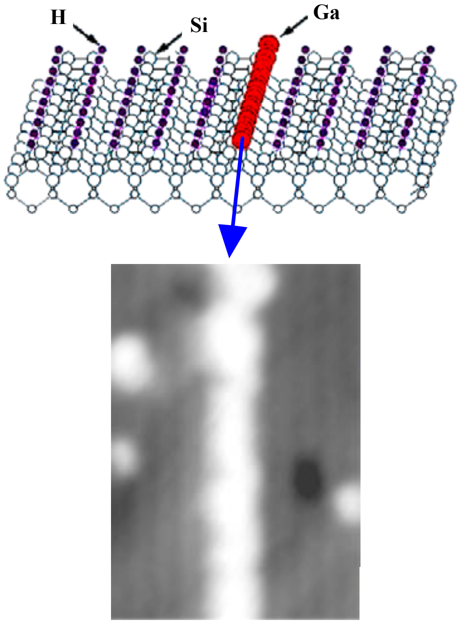
Selective Metallization: Physical Deposition

Aluminum (0.1 ML)



T.-C. Shen, C. Wang, and J. R. Tucker, *Phys. Rev. Lett.* 78, 1271 (1997).

Gallium



T. Hashizume, S. Heike, M. I. Lutwyche, S. Watanabe, K. Nakajima, T. Nishi and Y. Wada, *Jpn. J. Appl. Phys*, 35(8B), Part 2, L1085-L1088 (1996).

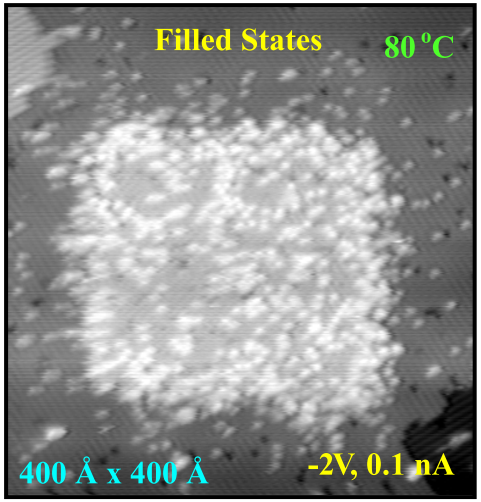
Selective Metallization: CVD of Gold

IBM Collaborators: Phaedon Avouris and Paul Seidler

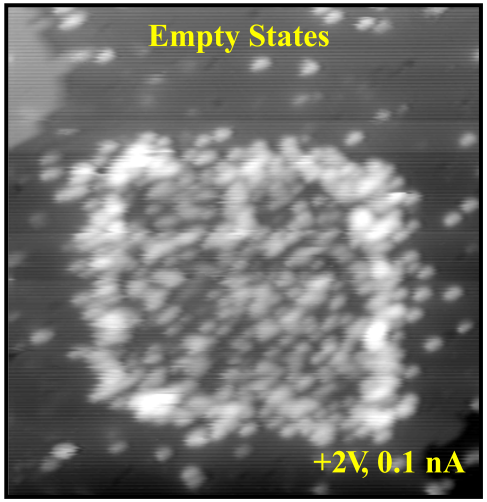
Selective Au depostion:

1. Room T Dose: Incomplete Dissociation
2. High T Dose: Metal Deposition

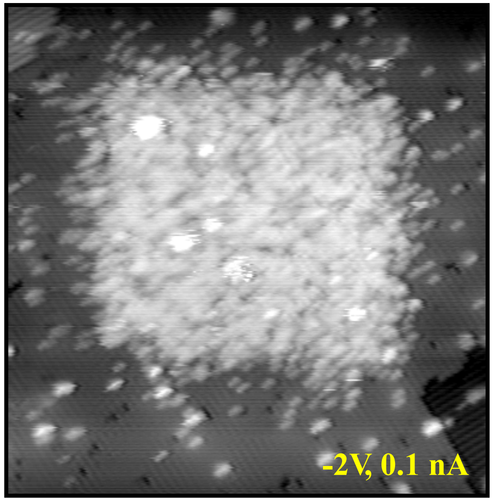
After 10L Dose



After 10L Dose



After 20L Dose

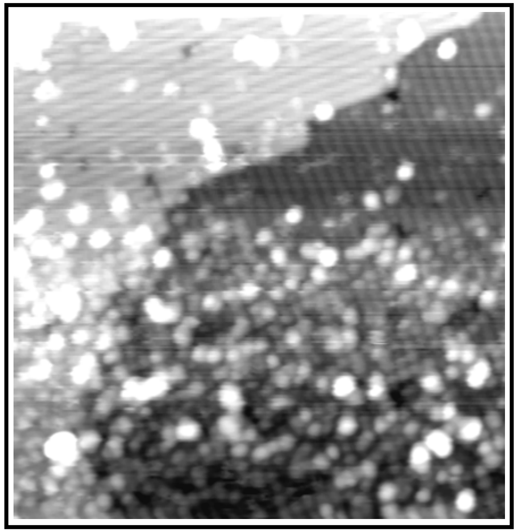


Precursor Molecule: $CH_3CH_2AuP(CH_3)_3$

Selective Metallization: CVD of Aluminum

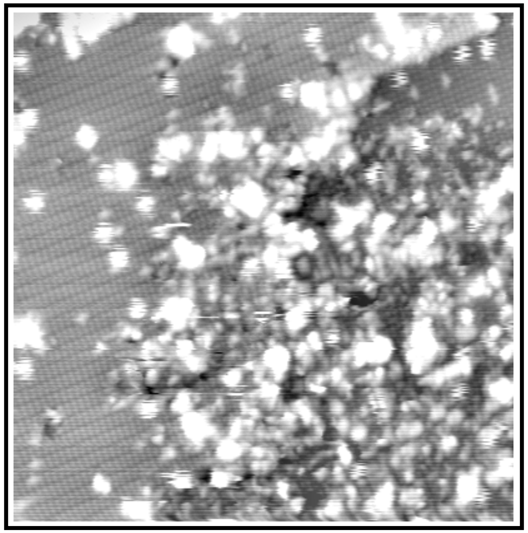
Novel amine-stabilized alane Al precursor developed by Dr. Hyungsoo Choi, Beckman Institute

0.2 L Dose at 200 °C



2x2 Al Overlayer

0.5 L Dose at 200 °C

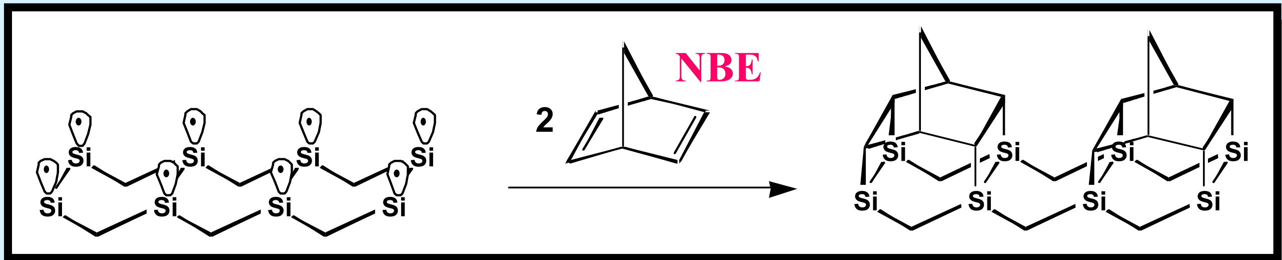


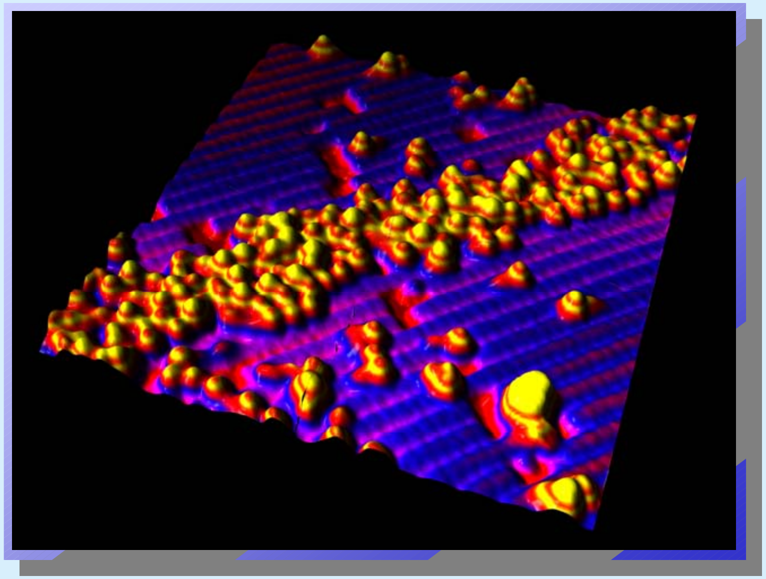
Disordered Al overlayer

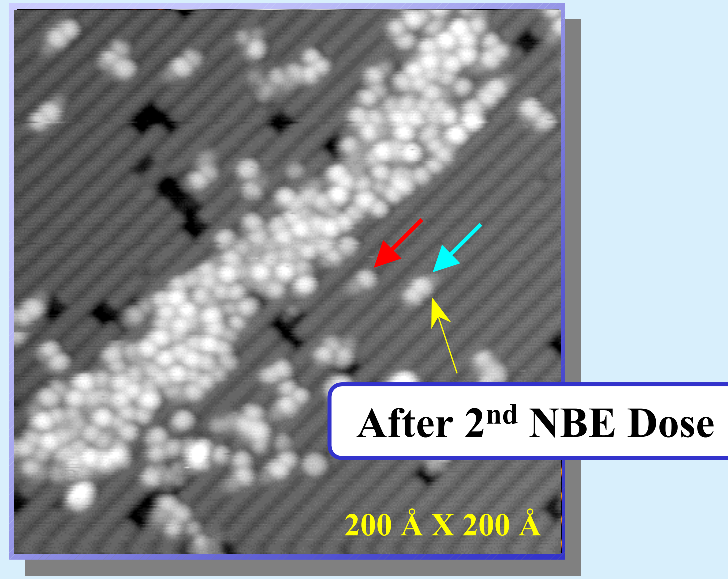
- To improve morphology for thicker layers, use $TiCl_4$ as a nucleating agent.
- Selective depositon of $TiCl_4$ has been demonstrated at room temperature.

Selective Molecular Adsorption of Norbornadiene on Silicon

G. C. Abeln, M. C. Hersam, D. S. Thompson, S.-T. Hwang, H. Choi, J. S. Moore, and J. W. Lyding,
J. Vac. Sci. Technol. B, 16, 3874 (1998).







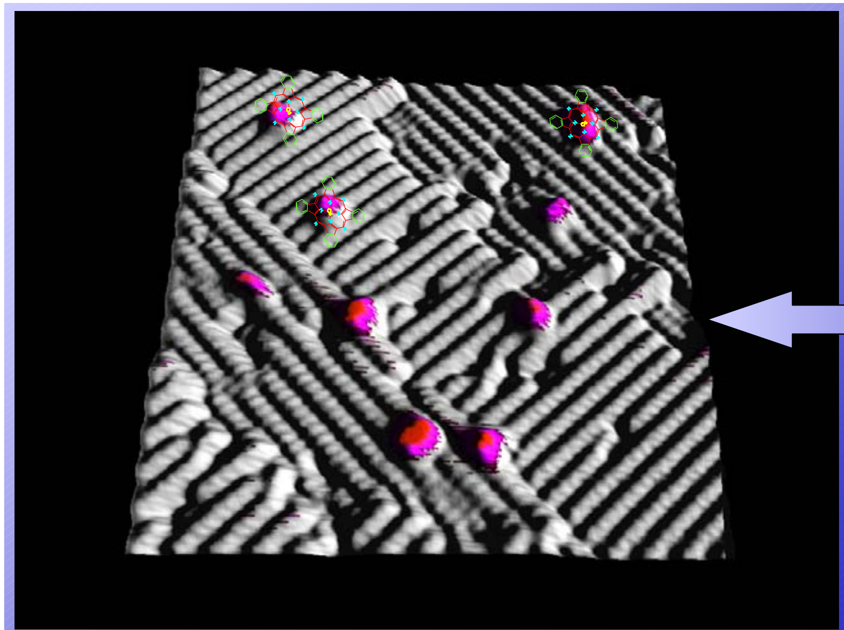
Norbornadiene (NBE) is conformationally predisposed to react with adjacent Si(100) dimers to form organosilicon "cage" structures ([2+2] cycloaddition reaction).

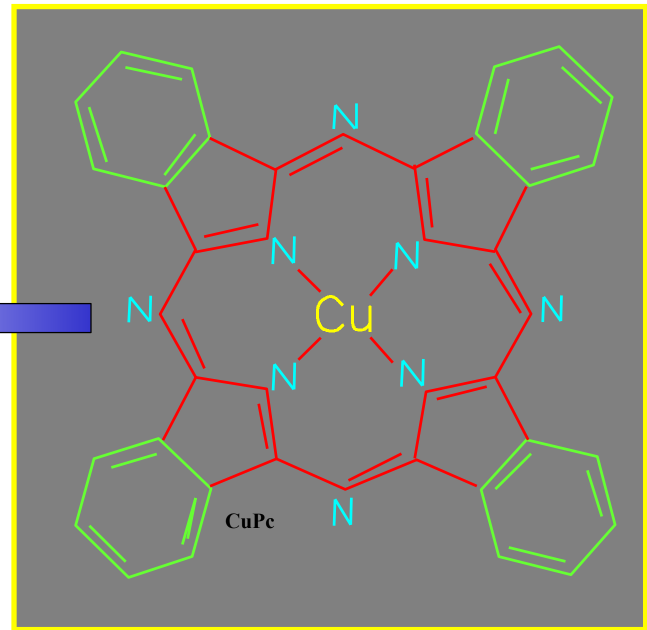
Department of Materials Science and Engineering, Northwestern University

Silicon-Based Molecular Nanoelectronics

A Bottom-Up Approach

Dose Surface with Molecules like Copper Phthalocyanine



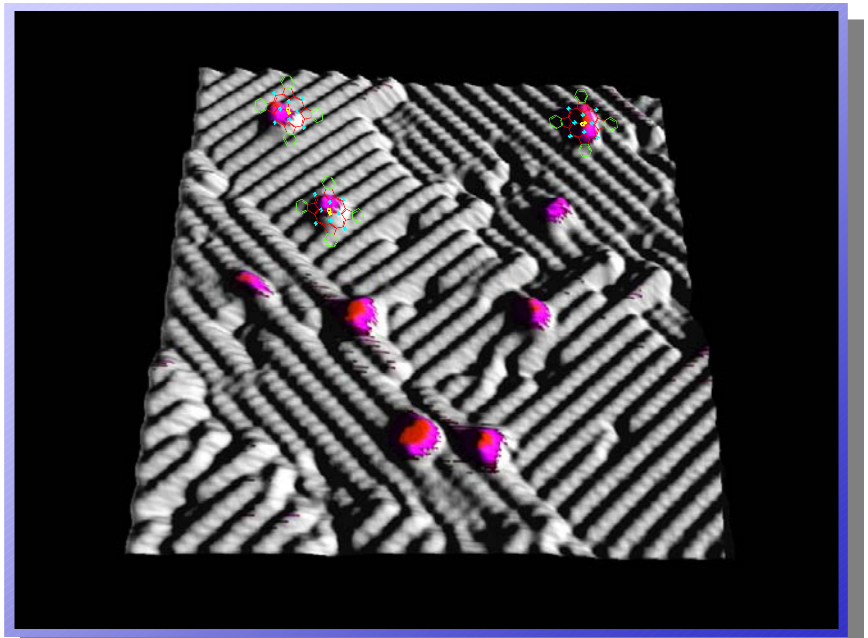


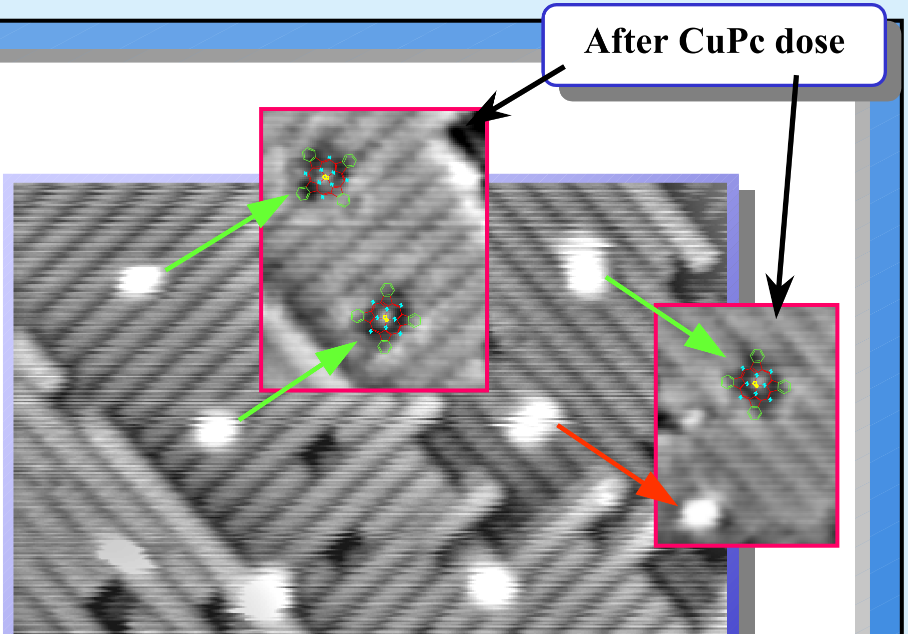
Department of Materials Science and Engineering, Northwestern University

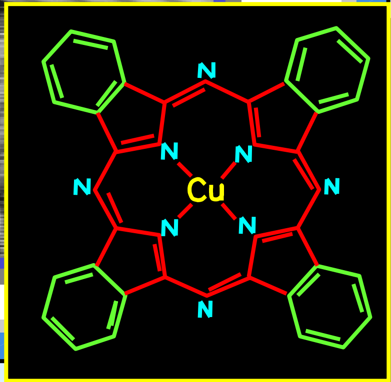
Silicon-Based Molecular Nanoelectronics

A Bottom-Up Approach

Dose Surface with Molecules like Copper Phthalocyanine





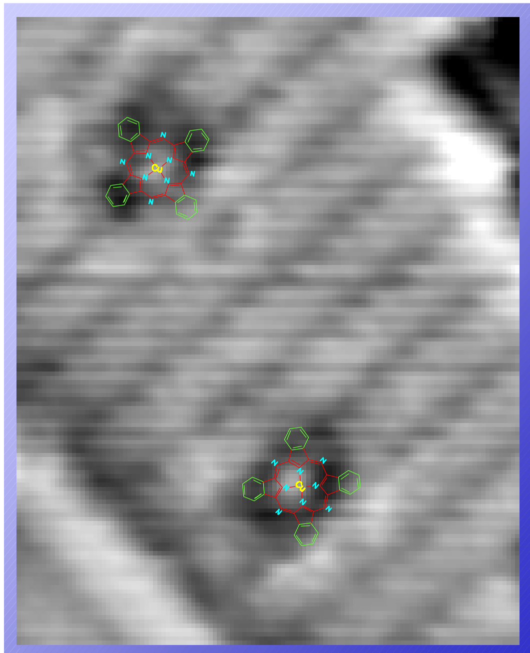


Department of Materials Science and Engineering, Northwestern University

Copper Phthalocyanine

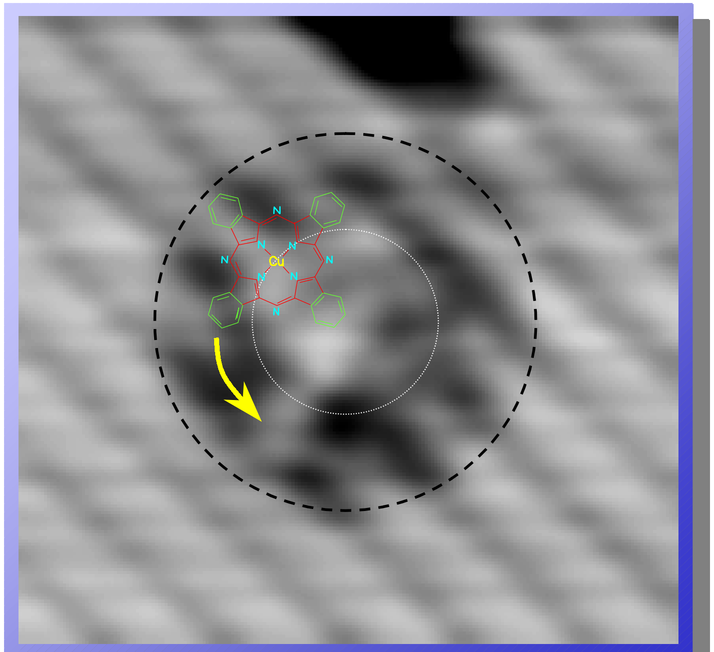
Stationary vs Rotating Molecules

Stationary



CuPc bonded by central Cu atom.

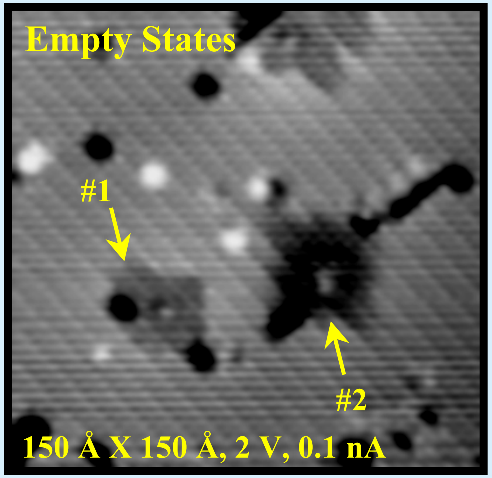
Rotating

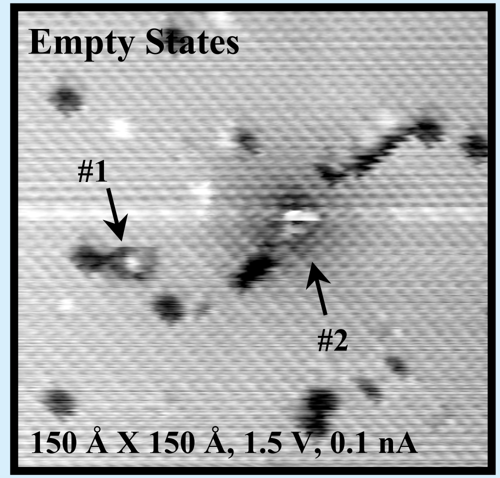


NH_3-reacted CuPc forms weak bond via outer benzene ring.

Evidence of Molecular Rotation

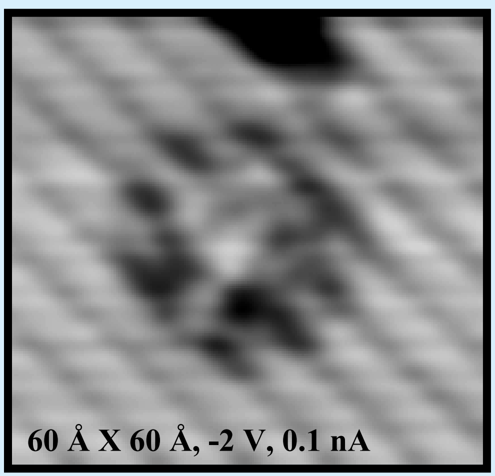
CuPc →

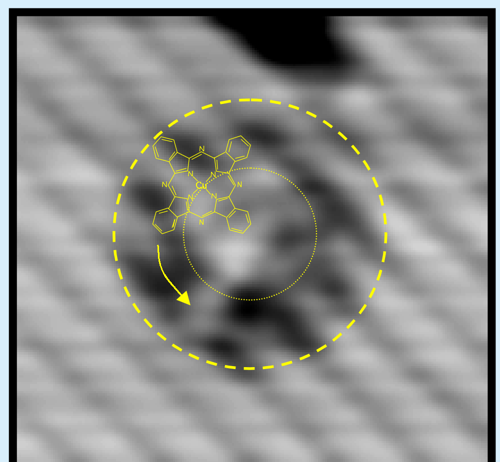




CuPc can either be fixed or rotating on the surface.

CuPc + NH_3 →

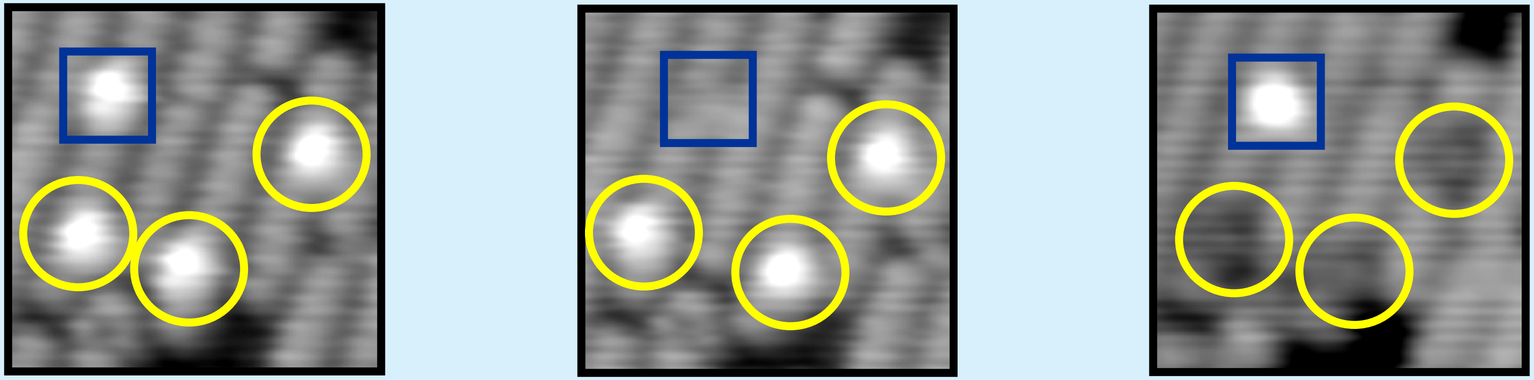




NH_3-CuPc always rotates on the surface.

Jann-Teller effect may be playing a role.

Individual NBE Molecules on Si(100)



(45 Å)^2 filled states image of four depassivated sites

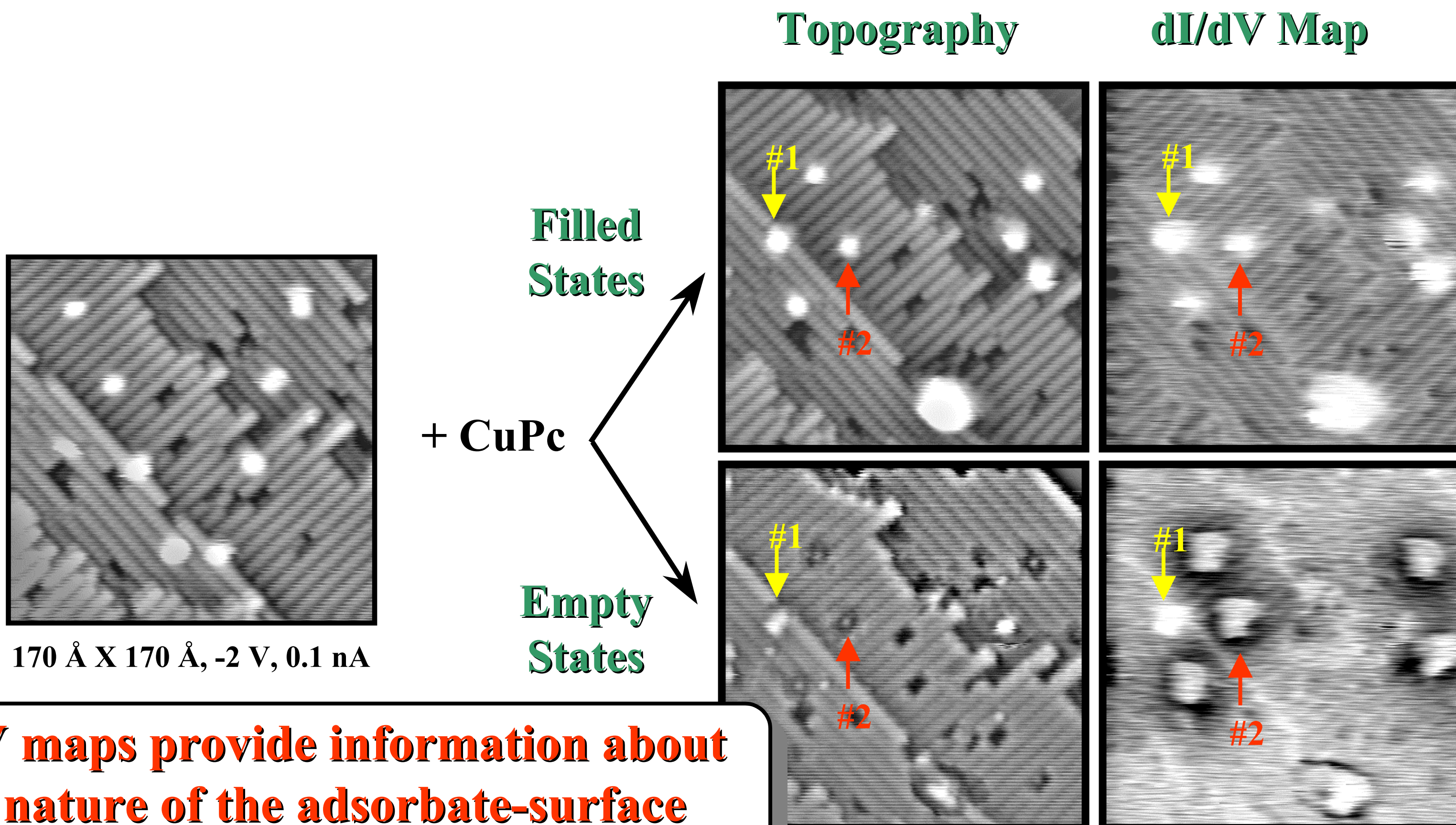
Filled states image after norbornadiene dose

Empty states image after norbornadiene dose

- STM images are a convolution of topography and electronic structure.
- Multi-bias imaging can sometimes distinguish different adsorbed molecules.
- In this case, the boxed molecule behaves like water, whereas the circled molecule is presumably norbornadiene (NBE).

STM spectroscopy can provide deconvolved information about electronic structure.

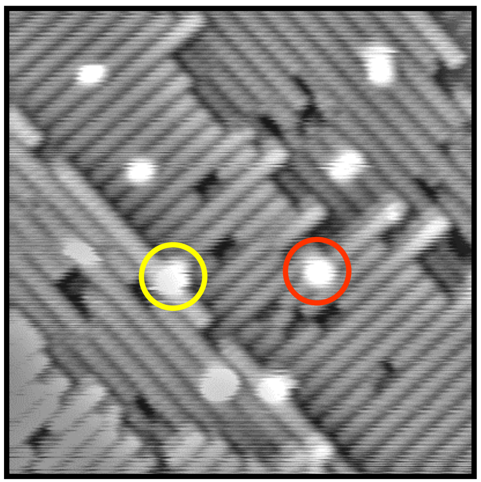
Copper Phthalocyanine - Spectroscopic Behavior



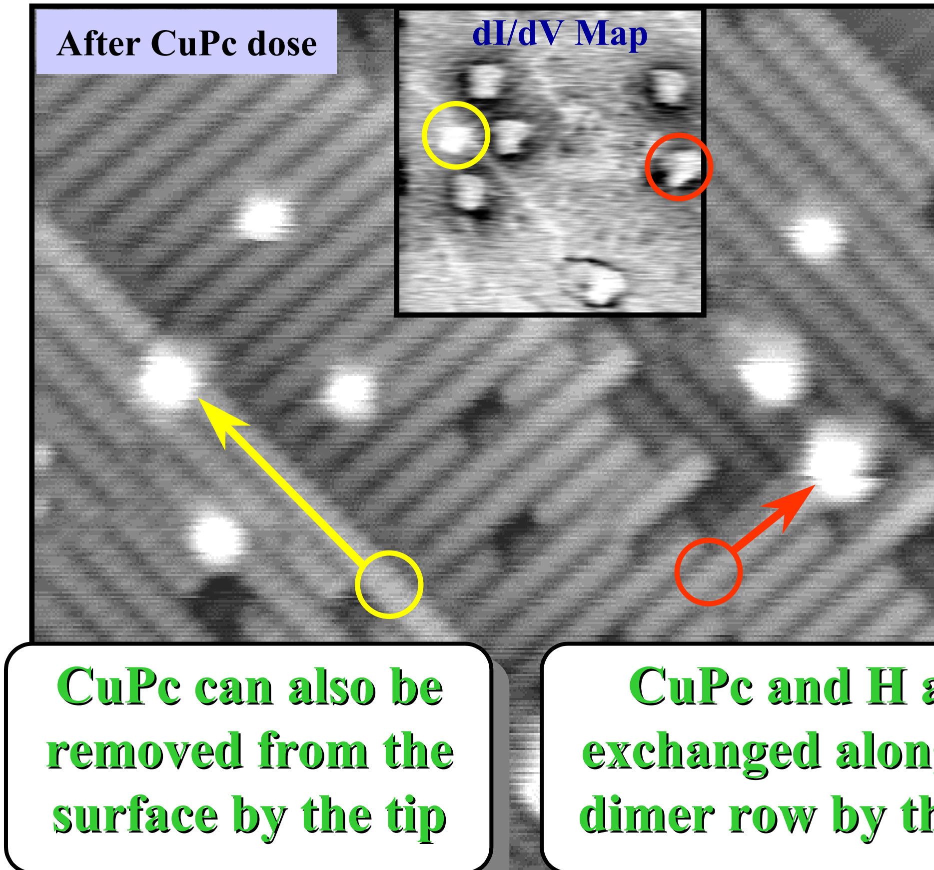
170 Å X 170 Å, -2 V, 0.1 nA

dI/dV maps provide information about the nature of the adsorbate-surface interaction (e.g., charge transfer)

Copper Phthalocyanine – Tip Induced Motion



Before CuPc dose

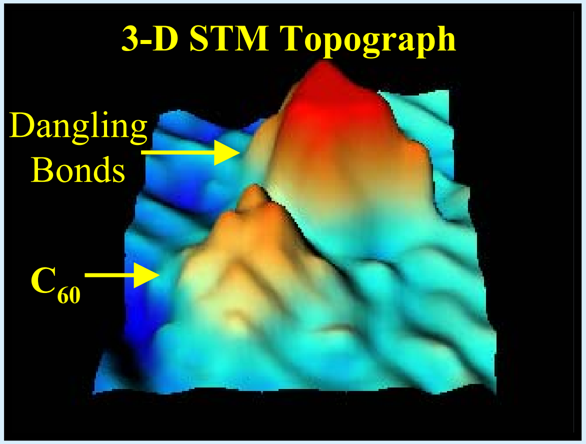


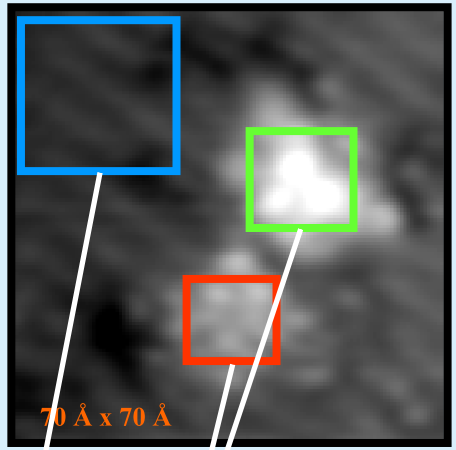
CuPc can also be removed from the surface by the tip

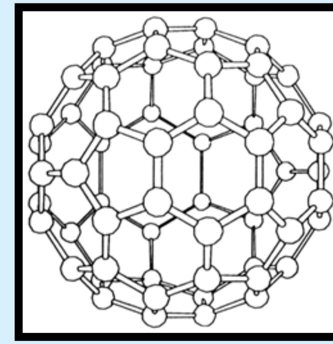
CuPc and H are exchanged along the dimer row by the tip

Single Molecule Spectroscopy

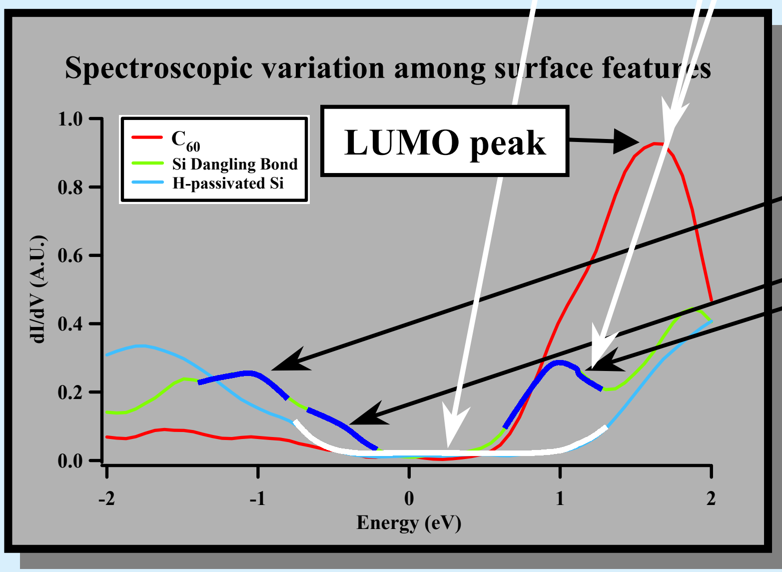
C_{60} - A Case Study

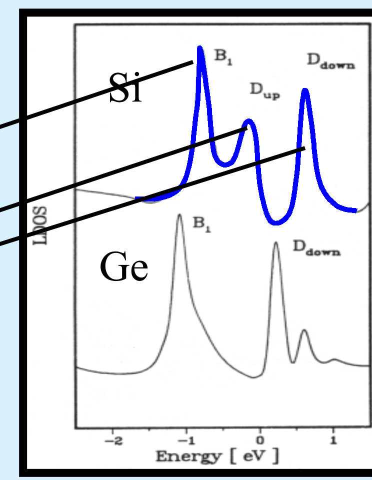






Structure of C_{60}

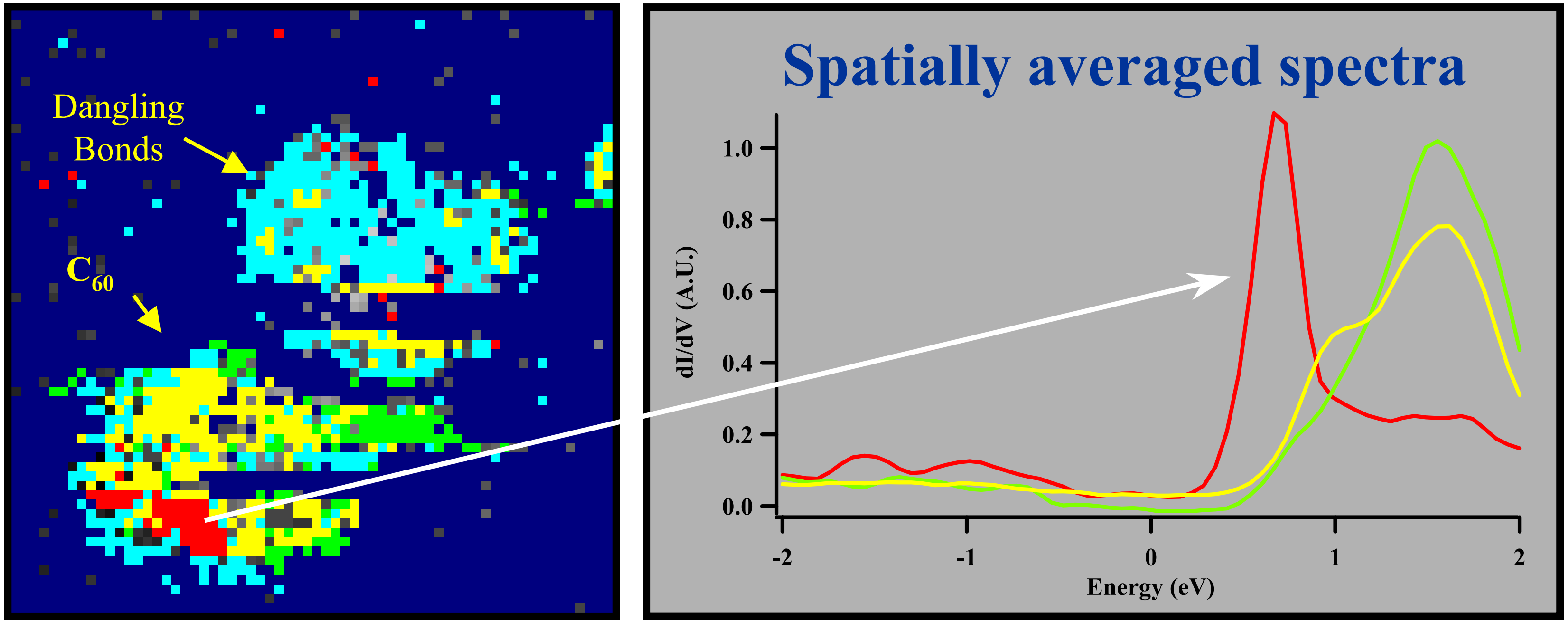




Calculated local density of states for Si(100)

J. Pollmann, P. Kruger, and A. Mazur, *JVST B*, 5, 945 (1987).

Intramolecular Spectroscopy of C_{60}

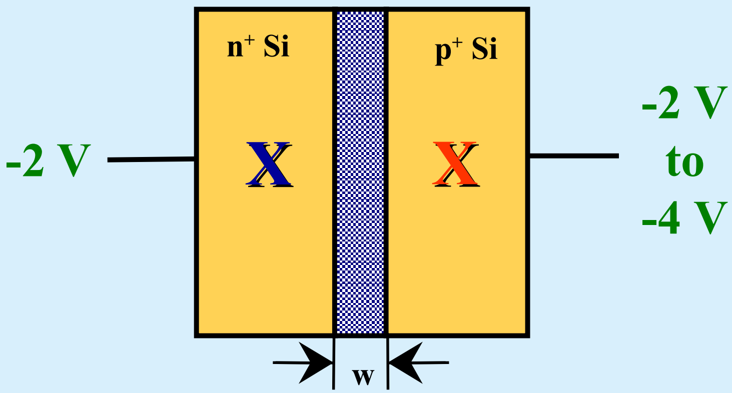


Use pattern recognition algorithm which analyzes 3D data set in energy space to identify electronically distinct regions.

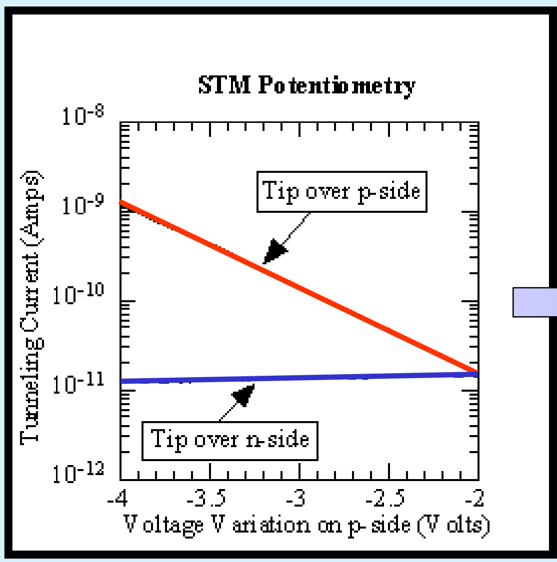
Department of Materials Science and Engineering, Northwestern University

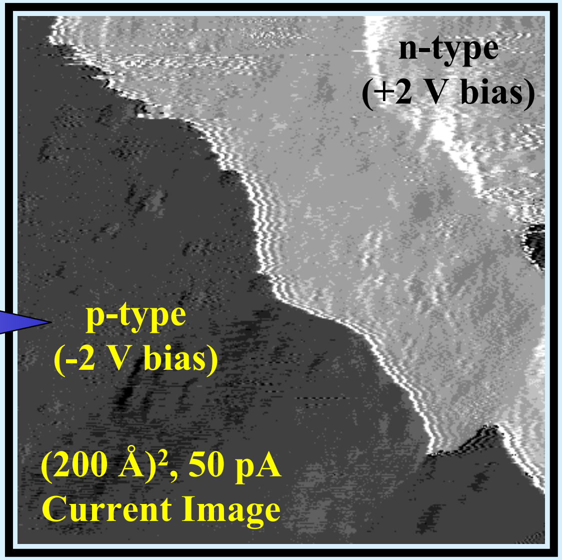
Location/Registration of Nanostructures

M. C. Hersam, G. C. Abeln, and J. W. Lyding, *Microelectronic Engineering*, 47, 235 (1999).



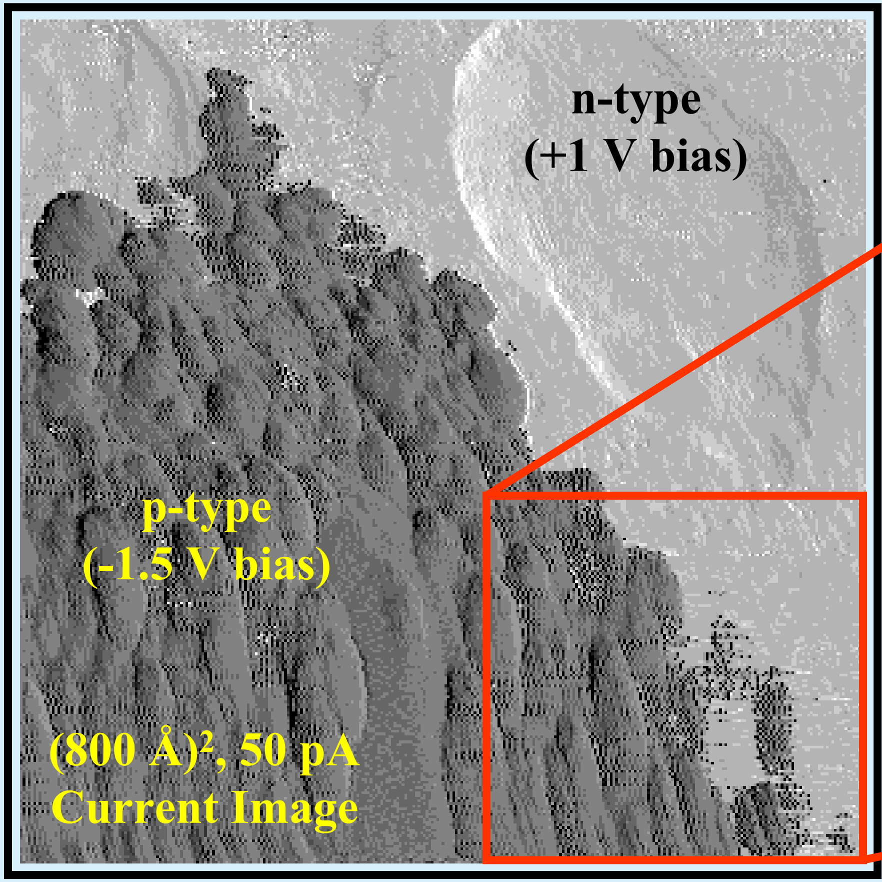
- Efficient location of nanostructures is critical for further processing after STM lithography is completed.
- Goal: Develop an efficient binary search routine.
- Idea: Use STM potentiometry to locate a pre-patterned *p-n* junction.

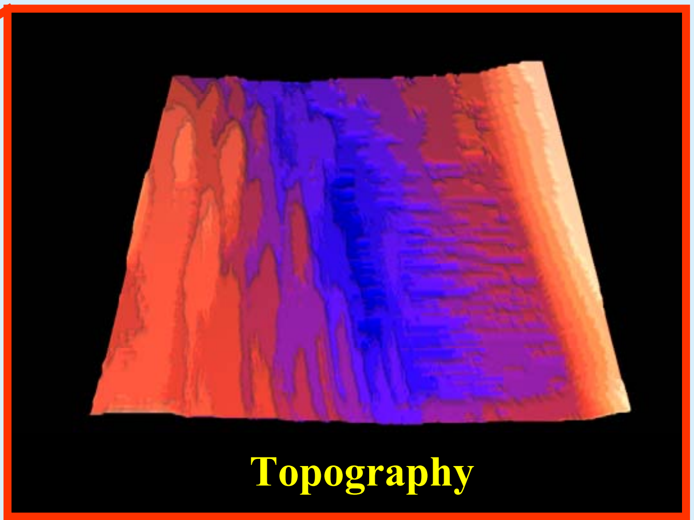




Delineation of a *p-n* junction after location.

STM Imaging of a *p-n* Junction



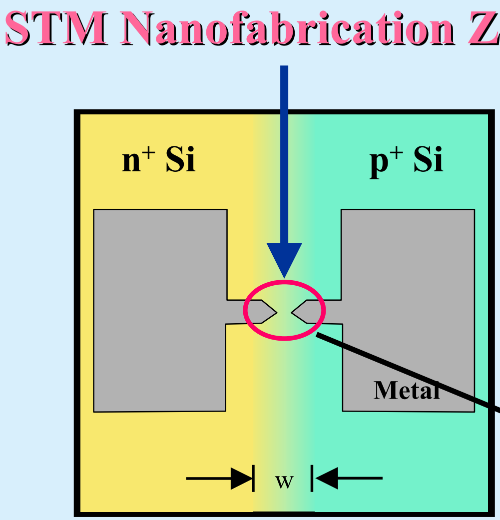


Substrate: Si(100), p-type, B-doped (~ 0.01 Ω-cm)

Processing:
1.) Phos. predep @ 1000°C for 10 min.
2.) Phos. drive @ 1000°C for 10 min.
3.) ~ 1000°C anneal in UHV for 1 min.

Electrically Contacting Nanostructures

p-n Junction Approach



p-n junction approach

- Compatible with UHV processing and H-passivation/depassivation schemes.
- Will enable potentiometry and spectroscopy for measuring nanoscale electronic structure.

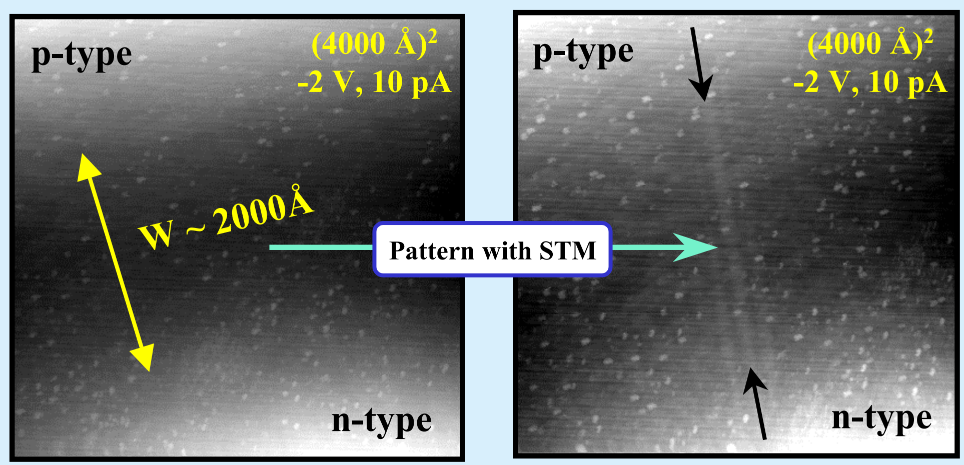


Image before patterning.

Image after patterning a line across the *p-n* junction.

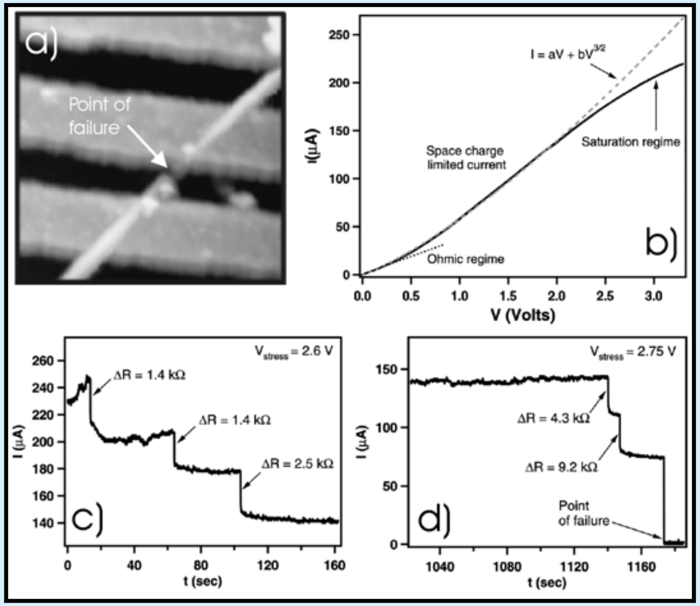
Substrate:
Si(100), n-type, As-doped (< 0.005 Ω-cm)

Processing:
1.) Boron predep @ 950°C for 1 hour
2.) ~ 1270°C anneal in UHV for 1 min.

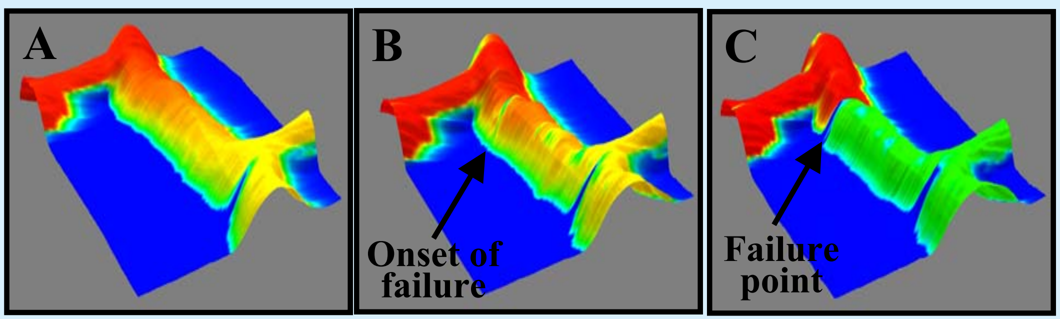
Nanoscale Charge Transport Measurements

- Electrical breakdown measurements on nanoscale systems
  - Gold nanowires (nanoscale electromigration)
  - Carbon nanotubes (quantized breakdown)
  - New molecules (e.g., DNA, thiol-derived SAMs)
  - Novel reliability techniques may be needed

Nanotube breakdown:



Gold Nanowire Failure:



M. C. Hersam, et al., *Appl. Phys. Lett.*, 72, 915 (1998).

Nanotube breakdown data is from: M. C. Hersam, et al., *Science and Application of Nanotubes*, editors: Tománek and Richard Enbody, Kluwer Academic Publishers, p. 223 (2000).

Acknowledgements

Postdoctoral Research Associate

Dr. Edward Foley

Graduate Students

Michael Arnold
Rajiv Basu
Elizabeth Fabbroni
Mark Greene
Reagan Kinser
Matthew Such

Undergraduate Students

Andrew Baluch
Meghan Campbell
Liam Cavanaugh
Christopher Horst
Sai-Pong Leung

Funding provided by:

Arnold and Mabel Beckman Foundation
Army Research Office DURINT
National Science Foundation
Rockefeller Brothers Fund
Northwestern University NSEC, IBNAM