LEEM Studies of Growth of Novel Electronic Materials and Devices

Ruud Tromp

Thanks to:

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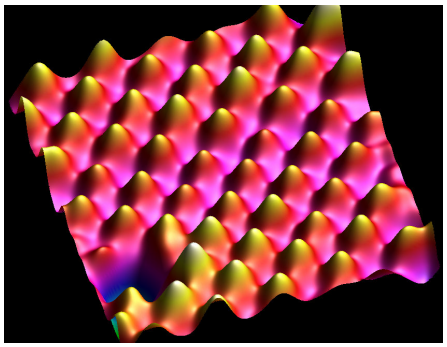
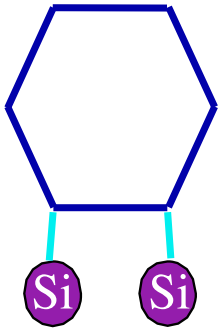
Emanual Tutuc

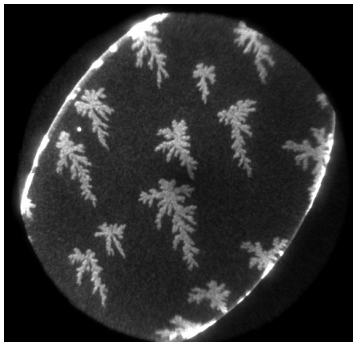
IBM

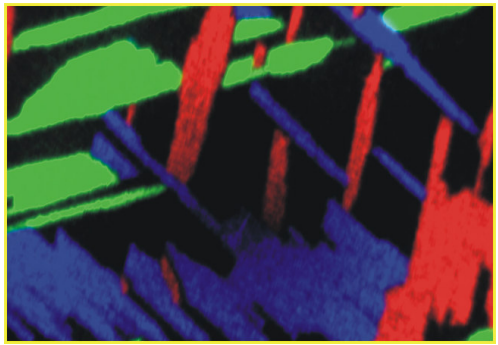
Overview

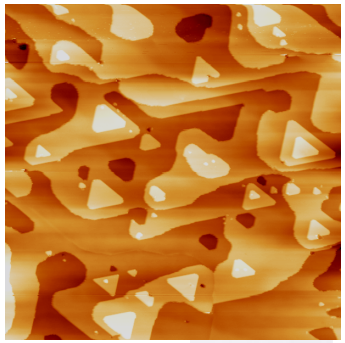
- Low Energy Electron Microscopy
- Growth of pentacene (Pn) on Si surfaces
- Growth of Nanowires – fundamental limits
- Surface Alloy Formation – Quantitative LEEM I-V



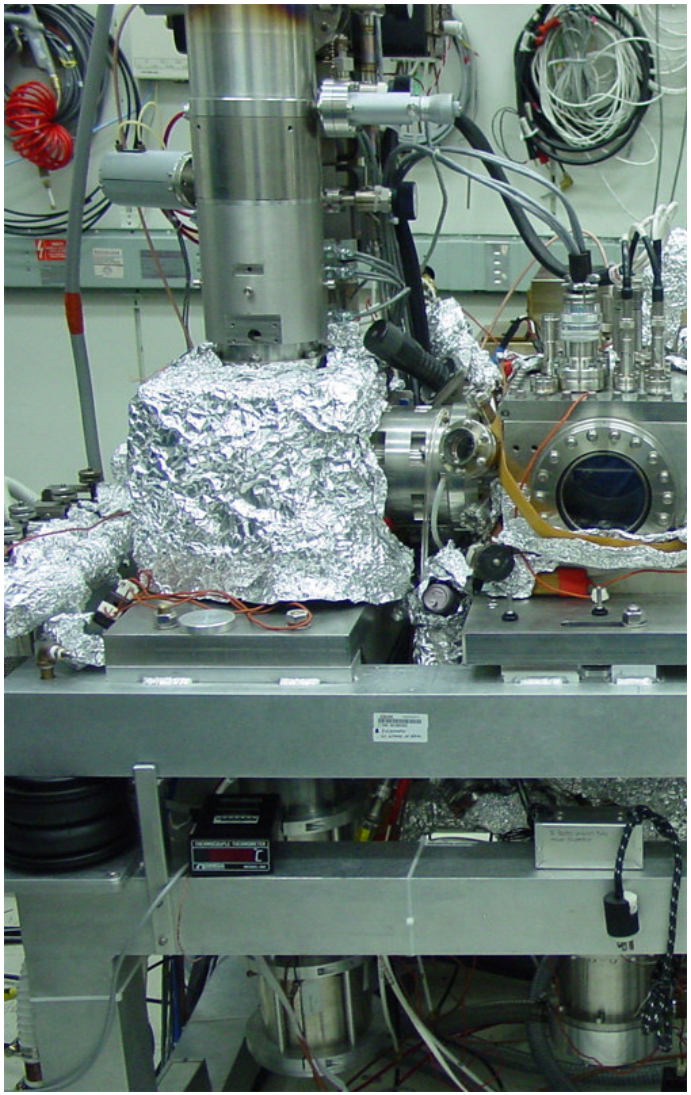


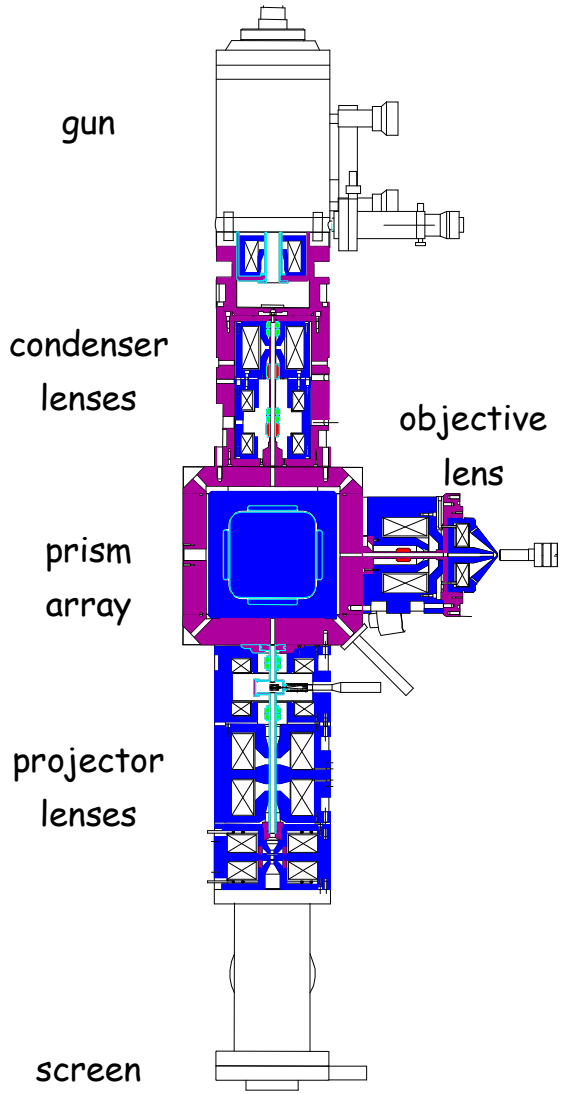


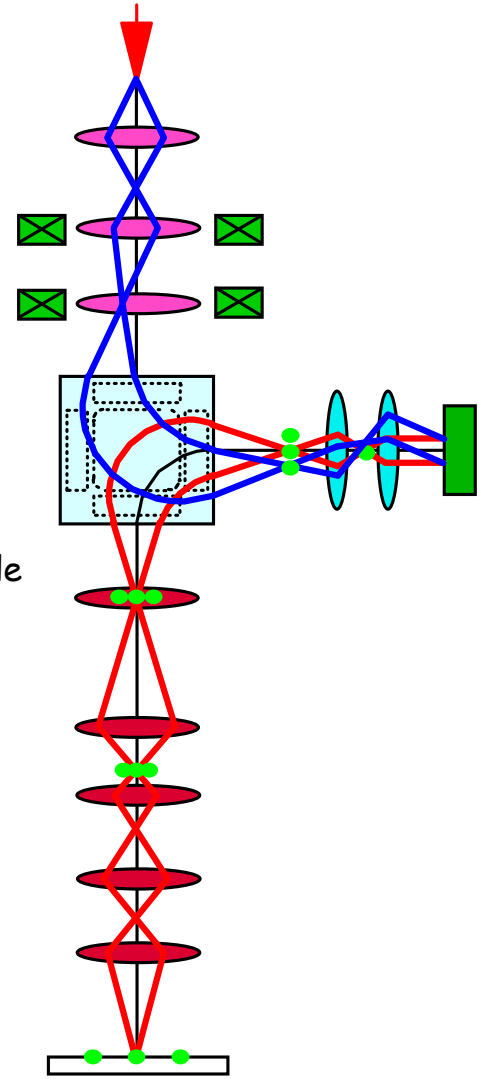




Low energy electron microscopy

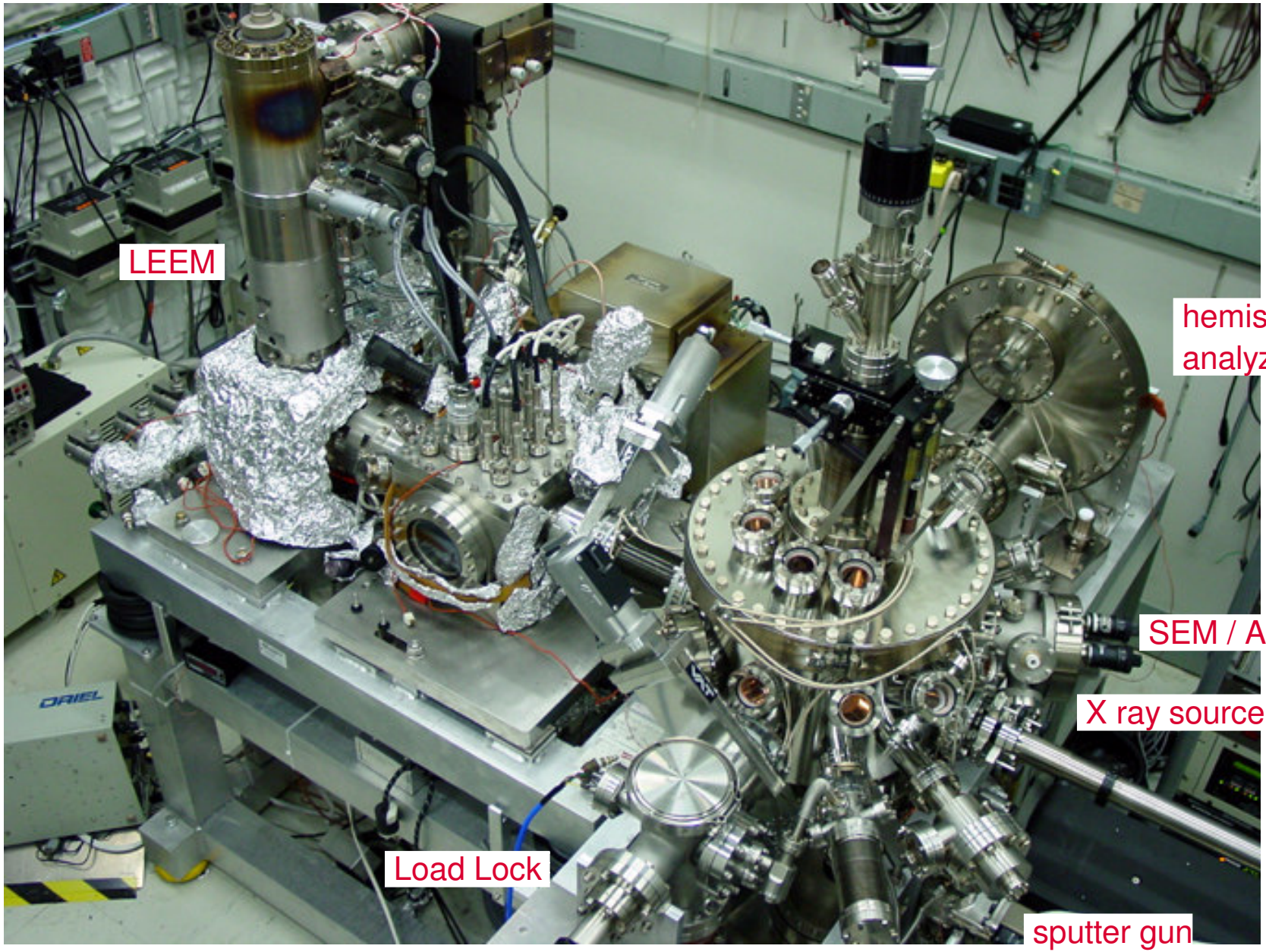




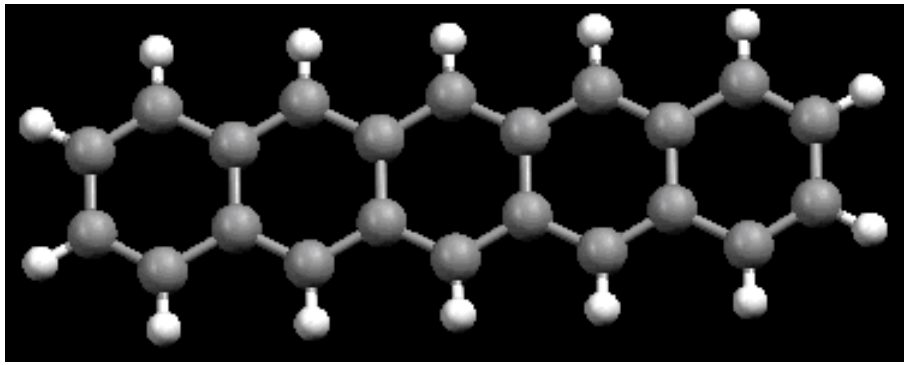


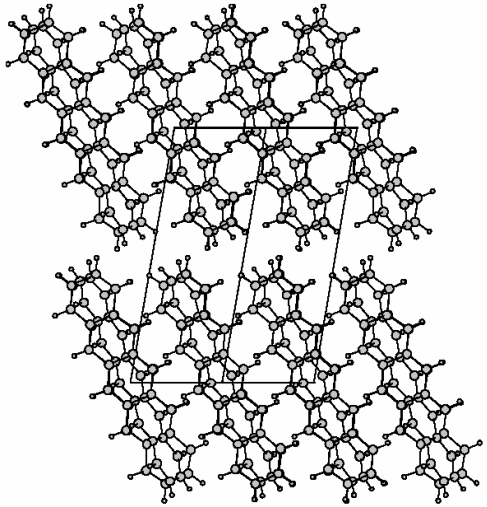
R.M.Tromp, M. Mankos, M.C. Reuter, A.W. Ellis, M. Copel
Surface Review and Letters **5** , 1189 (1998)

IBM Low Energy Electron Microscope

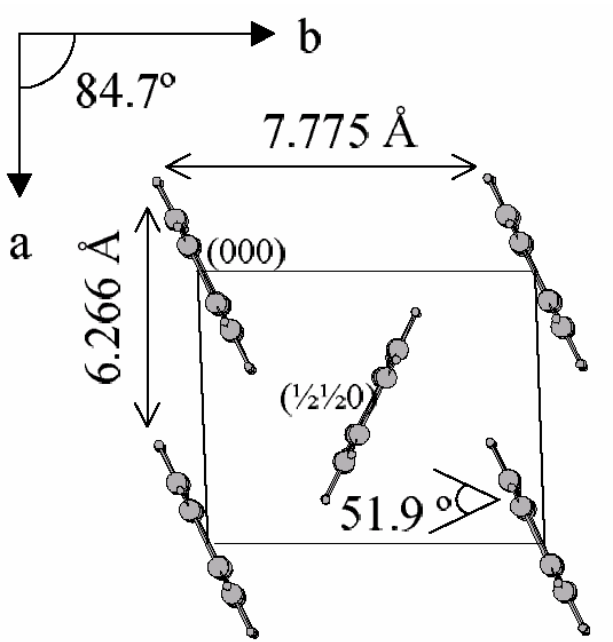


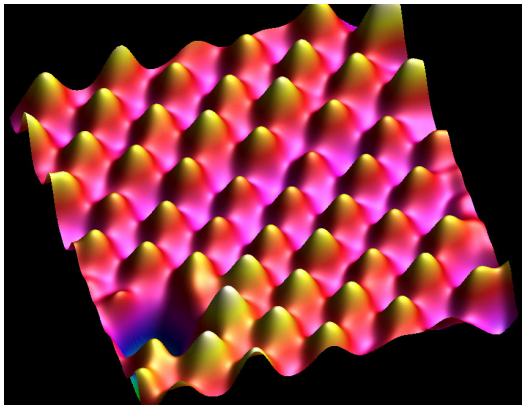
Pentacene crystal structure





Courtesy J. Sadowski



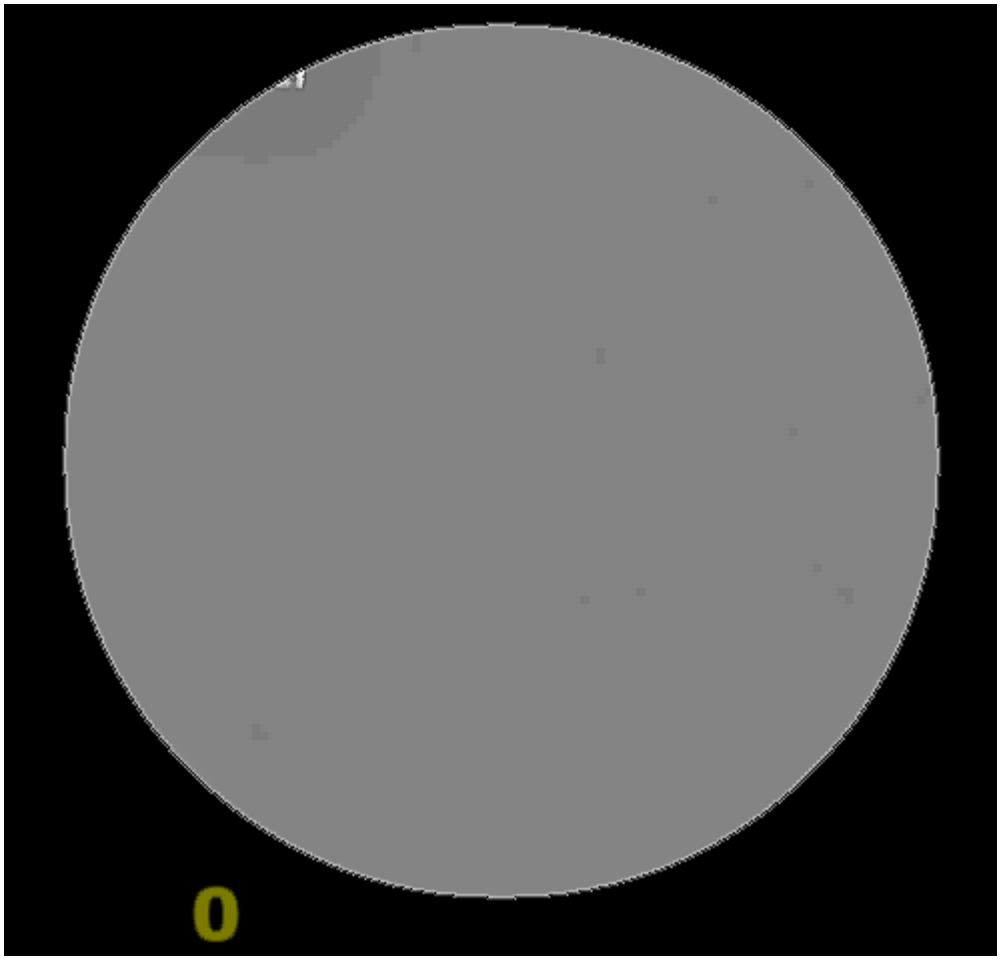


Courtesy Christine Corinne Mattheus

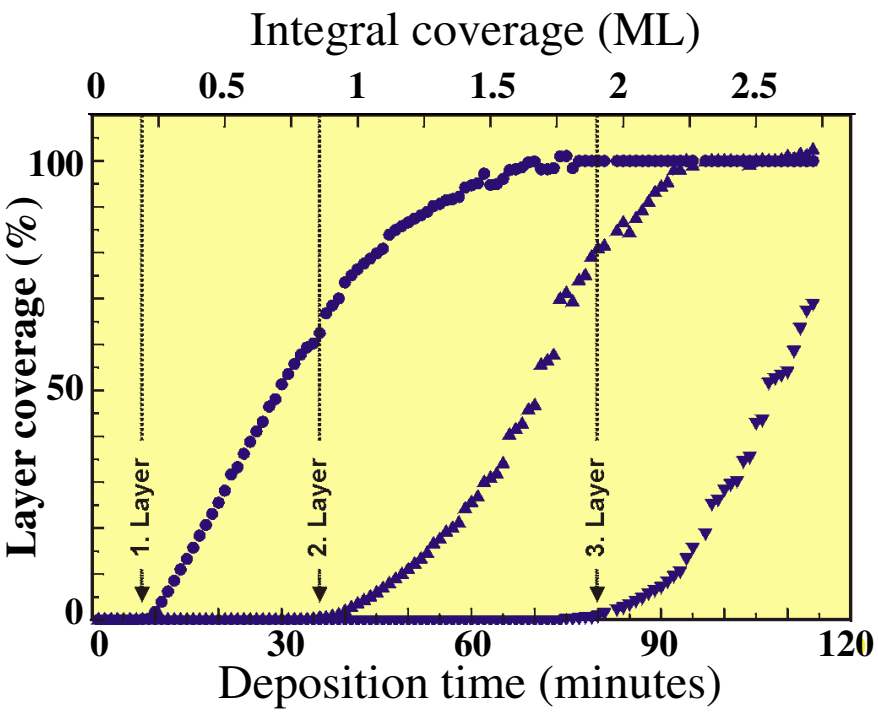
Triclinic

Two molecules per unit cell

Growth on clean Si

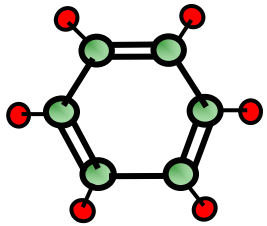


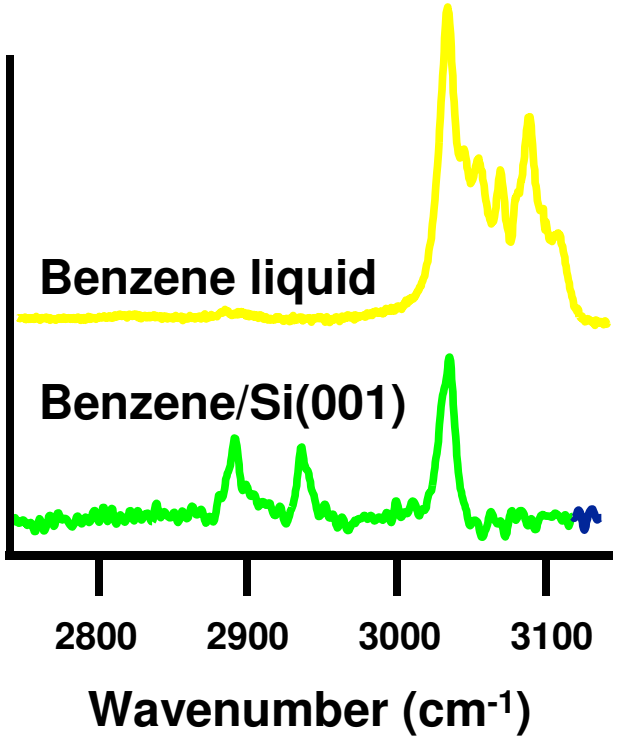
Field of view 65 µm
Room temperature
1 image/minute

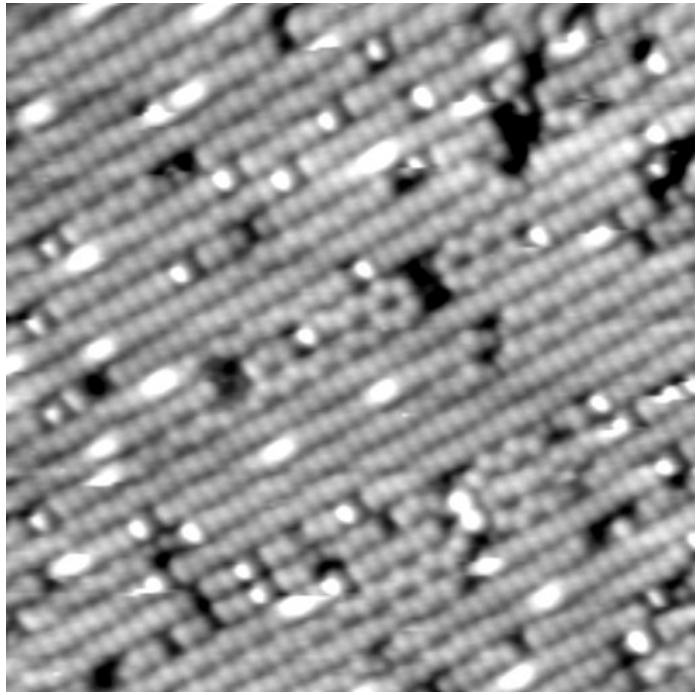


Meyer zu Heringdorf, F.-J.; Reuter, M.C.; Tromp, R.M. *Nature* **2001**, *412*, 517-520

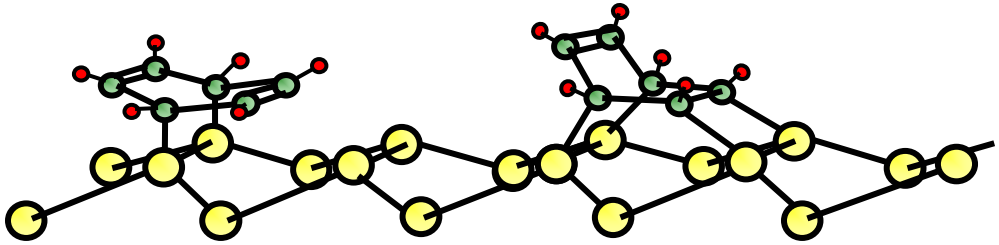
Aromatic and Pi-conjugated systems:





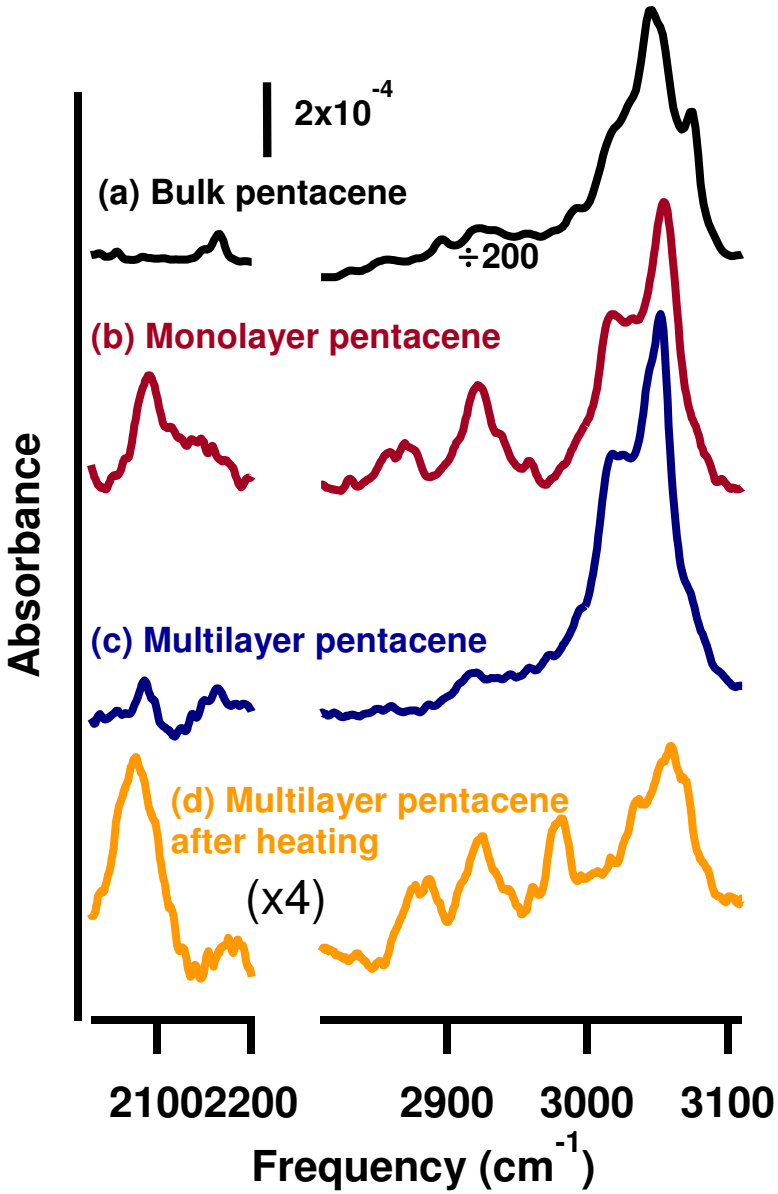


Multiple binding configurations



Benzene/Si(001) also undergoes transition from sp2 to sp3 hybridization
***Reversibly* adsorbs, desorbs**

Pentacene on Si(001): Infrared Spectra

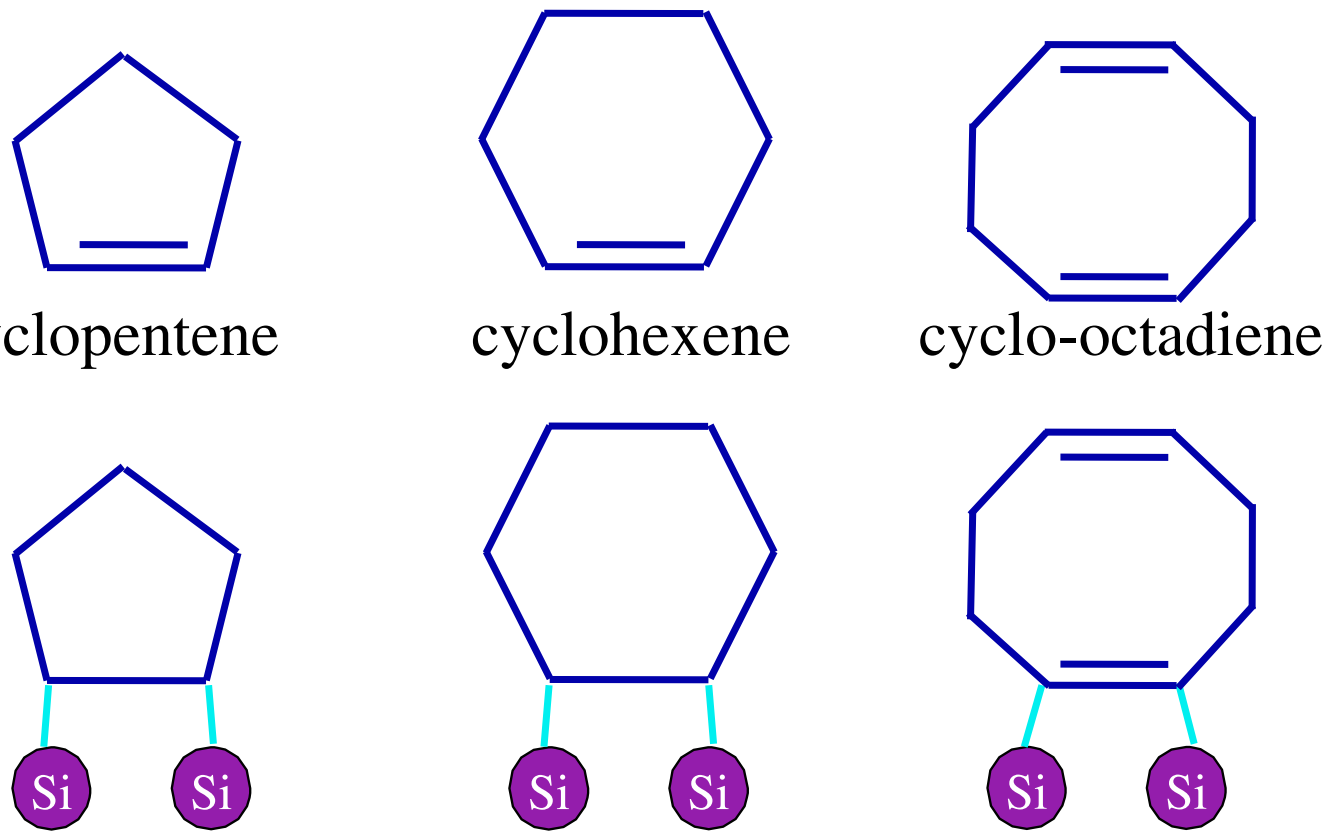


- Pentacene (bulk) shows no *sp*^{3} hybridized C-H stretching vibrations
- Monolayer coverage – peaks at 2091, 2870, 2922 cm^{-1} indicate Si-H and *sp*^{3} hybridized C-H bonds, also thermally stable
- Multilayer coverage – small Si-H peak, peaks above 3000 cm^{-1} are much larger than any below 3000 cm^{-1}
- Heating multilayer – broader Si-H peak, peaks almost identical to those of monolayer

Interfacial layer involves transition of some C atoms to sp3 hybridization and some dissocation. Layer appears to be thermally stable and *irreversibly* bound.

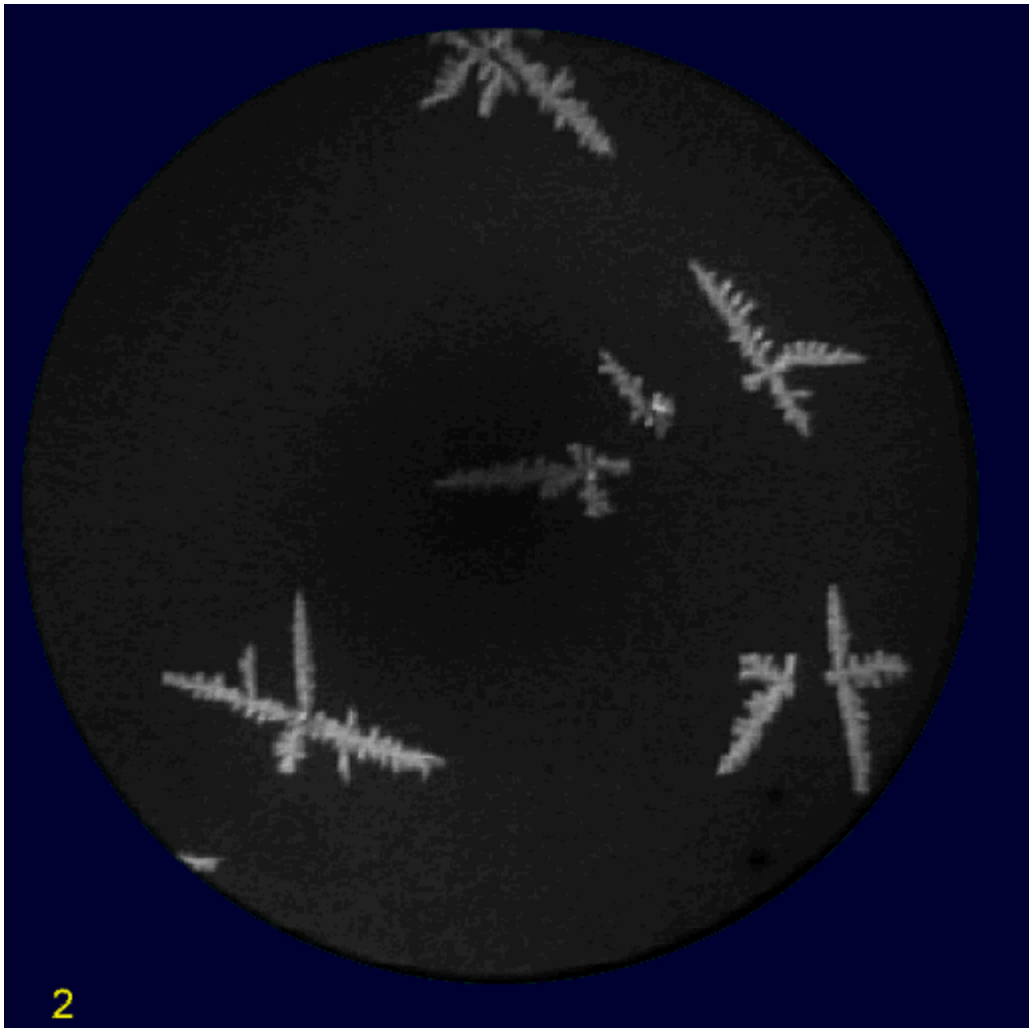
K.P. Weidkamp, C.A. Hacker, M.P. Schwartz, X. Cao, R.M. Tromp and R.J. Hamers,

Cyclo-addition reaction on Si

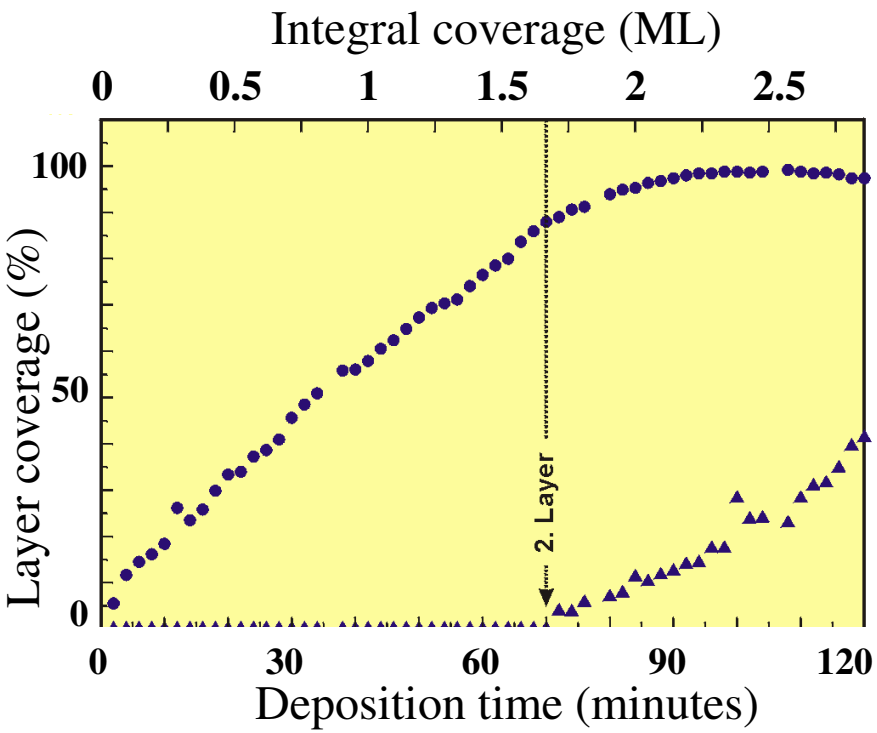


Organic surface termination renders Si surface inert, providing an ideal substrate for subsequent pentacene growth

Pentacene on Si/cyclohexene

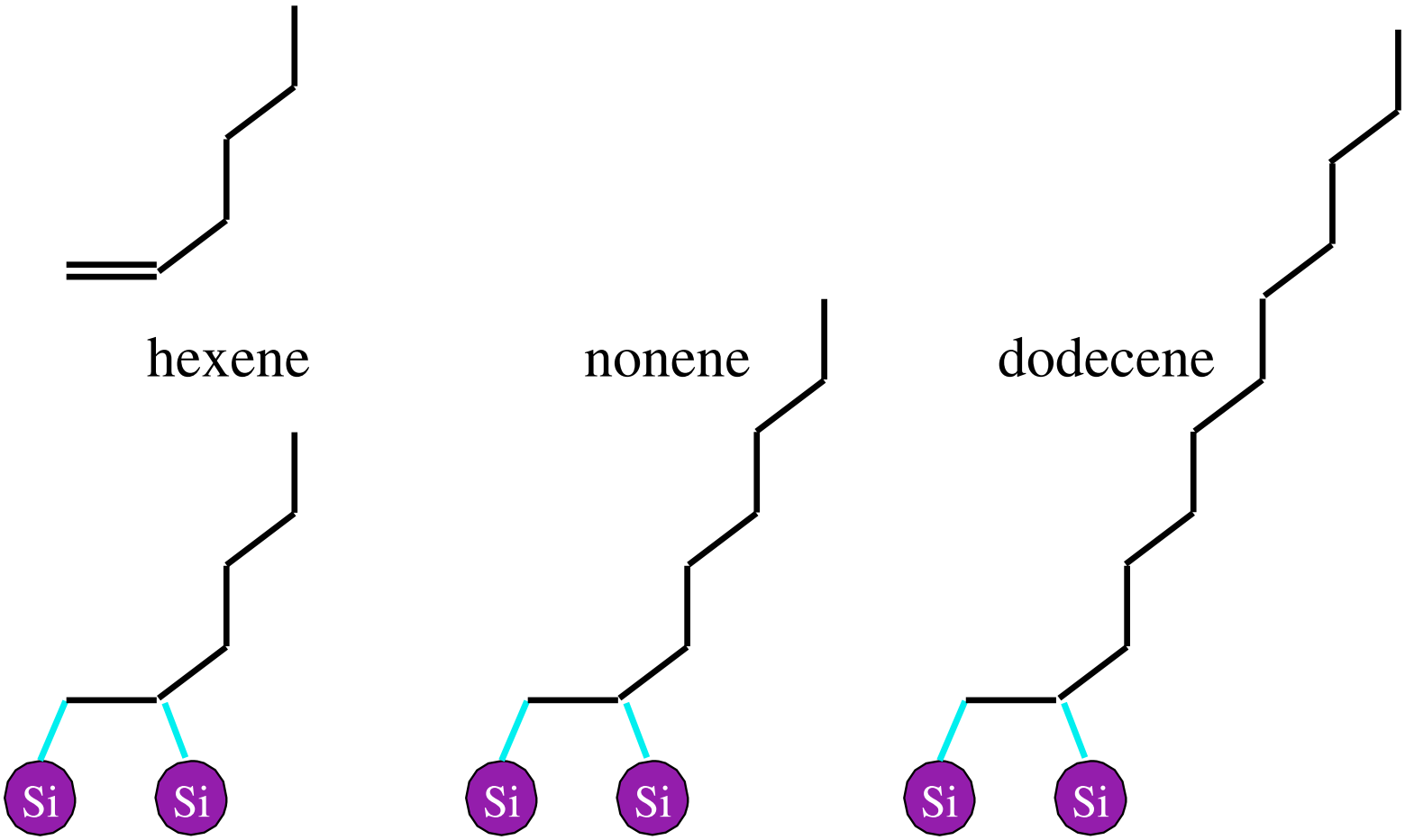


Field of view 65 µm
Room temperature
1 image/minute



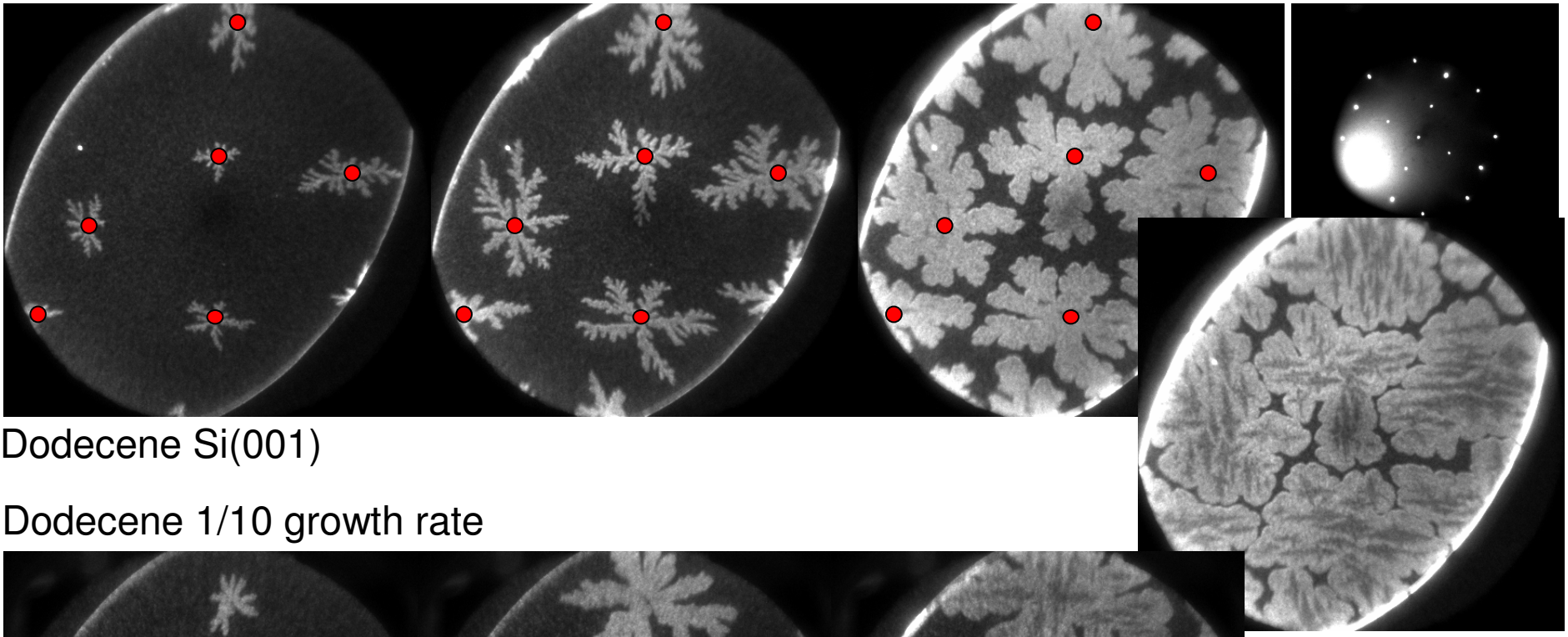
-J.; Reuter, M.C.; Tromp, R.M. *Nature* **2001**, *412*, 517-520

From cyclical molecules to chains



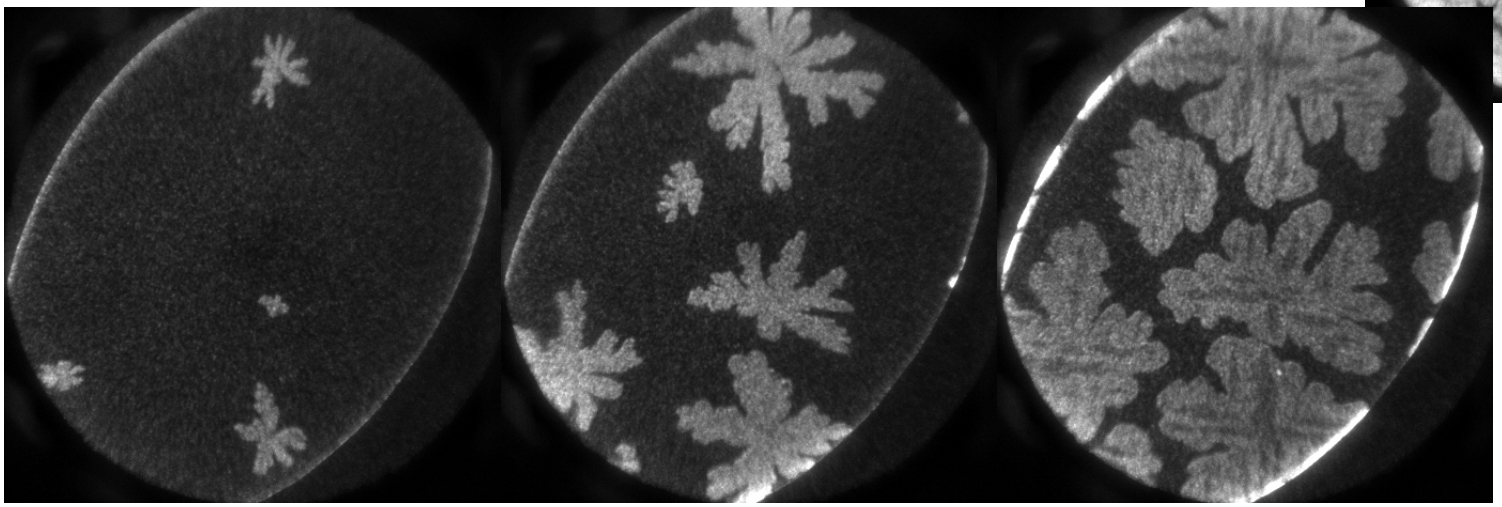
Chainlike molecules render Si surface inert, but affect diffusion and aggregation during pentacene growth

Dependence of fractal dimension on growth rate for dodecene: edge diffusion

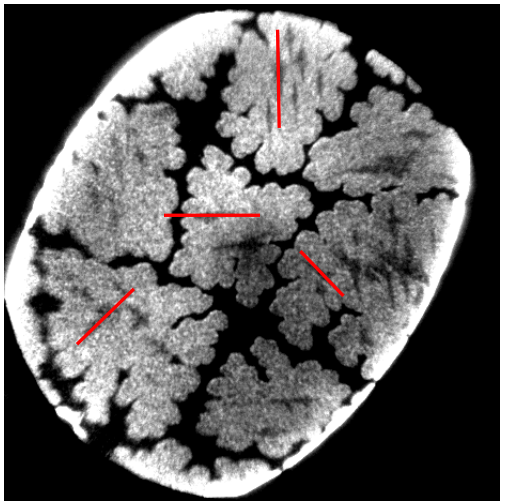


Dodecene Si(001)

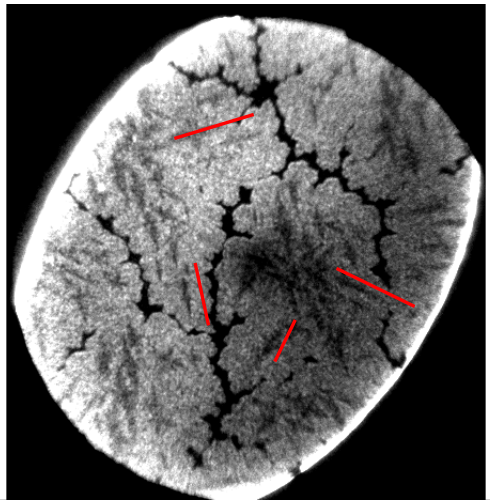
Dodecene 1/10 growth rate



Selection of azimuthal angles: Role of molecular species

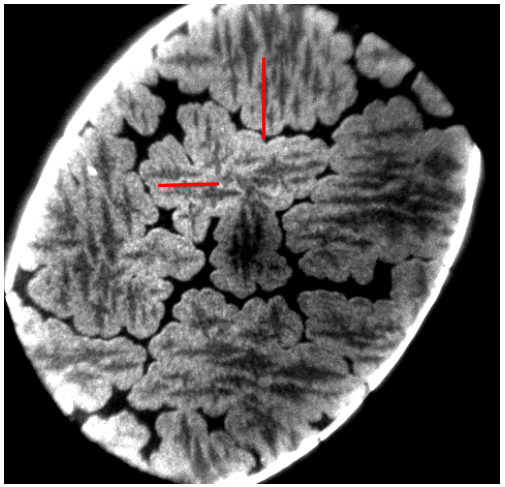


Cyclooctadiene

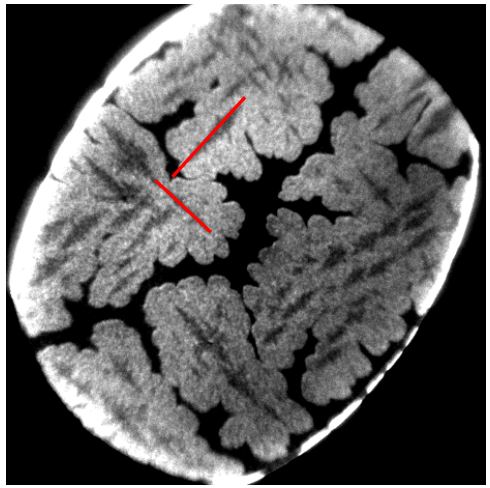


Hexene

Crystals at 45 degrees increments



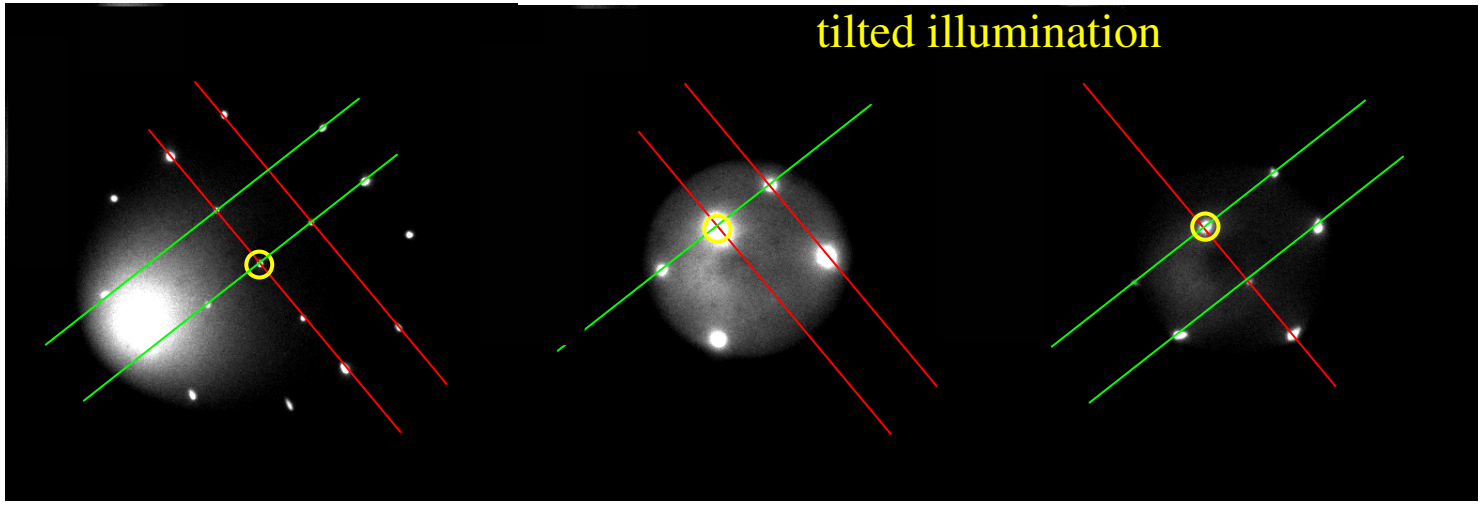
Dodecene on axis



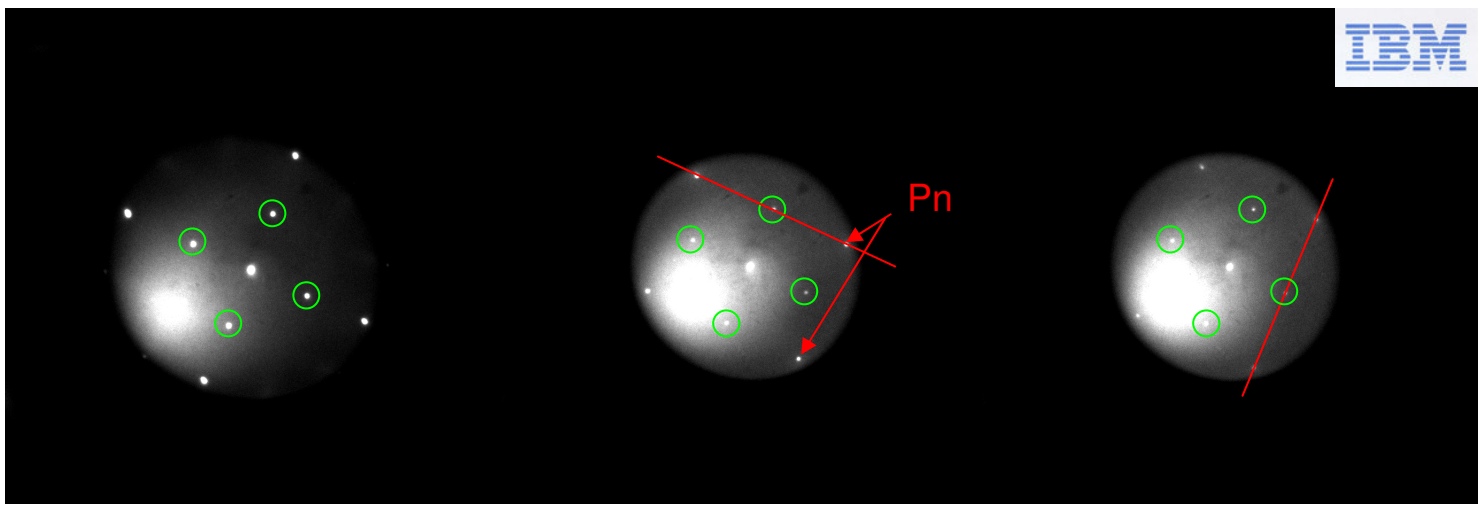
Dodecene off axis

Crystals at 90 degrees increments

Epitaxial growth of pentacene on Si: diffraction analysis



LEED 8/20 dodecene Si(001) on axis



Pentacene:
a = 0.627 nm
b = 0.777 nm
$\gamma = 84.7^o$

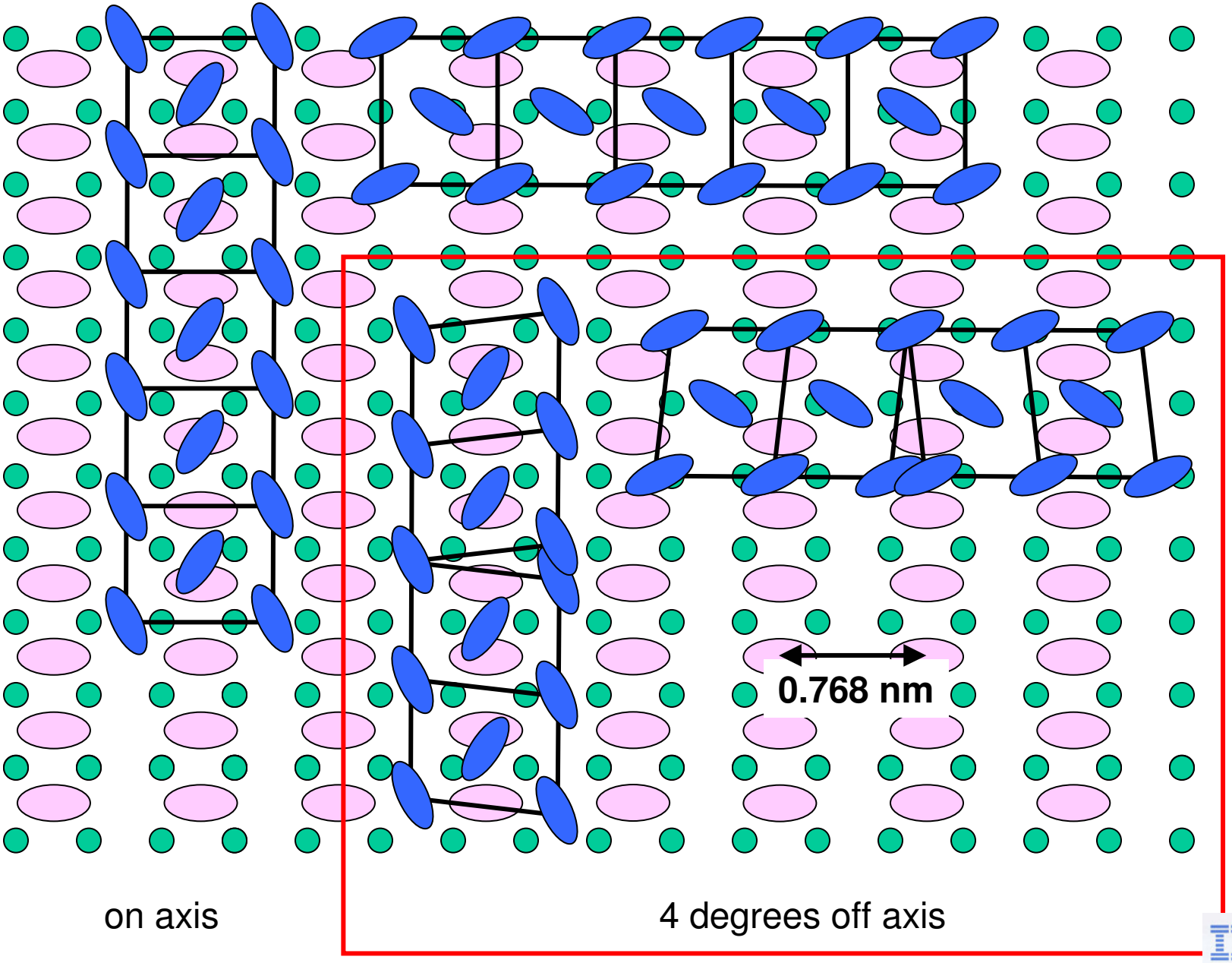
Si(001):
dimer-dimer: 0.384
row-row: 0.768

Mismatch ~ 1%

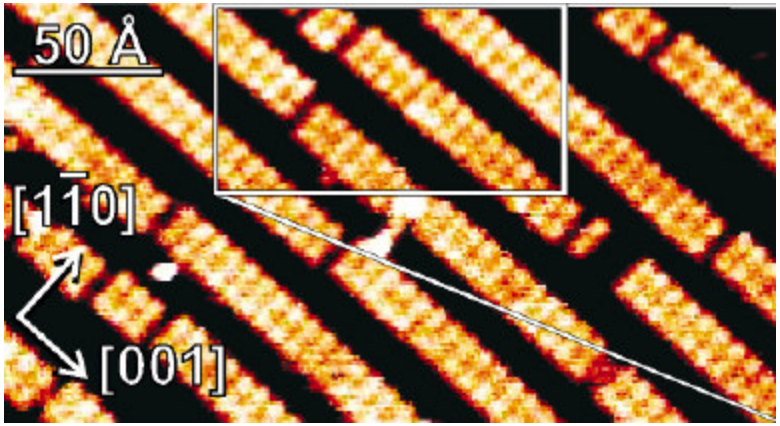
LEED 6/11 COD Si(001) on axis

Epitaxial growth, rectangular unit cell

PENTACENE /Si(001) EPITAXY



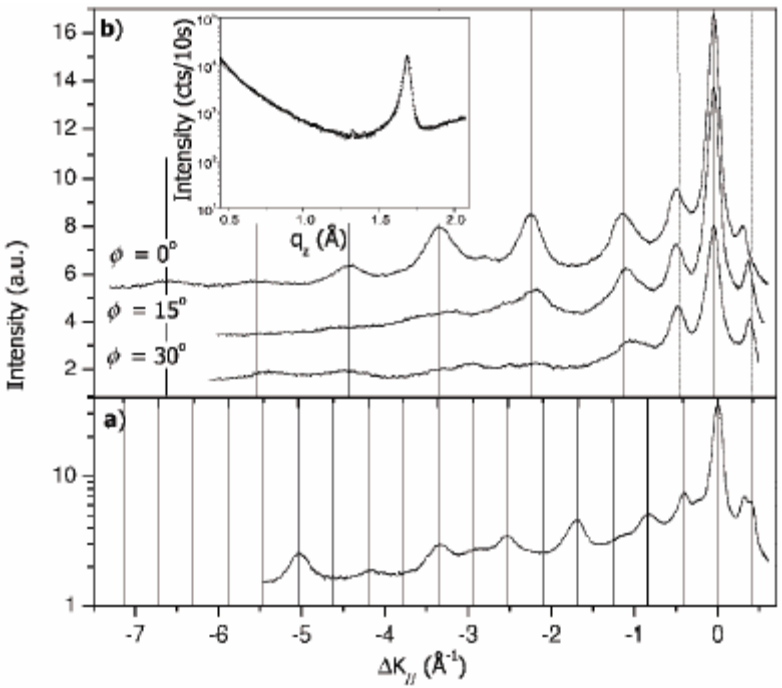
Pentacene on Metal Surfaces



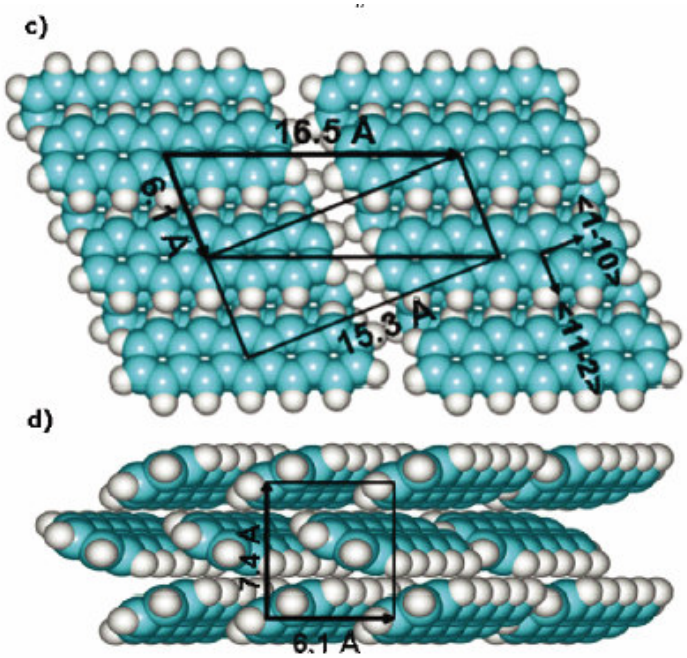
S. Lukas, G. Witte, Ch. Woell, PRL 88 (2002) 028301

On metals, molecules lie flat

Cu(110)



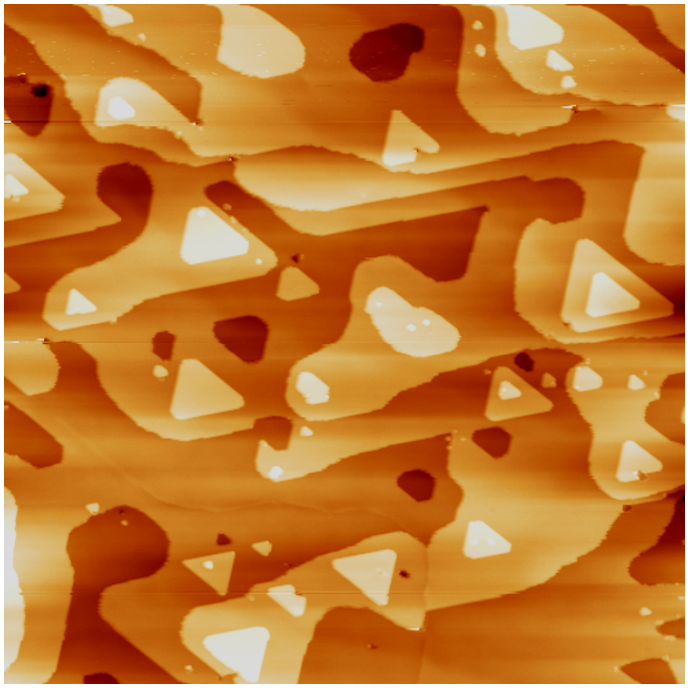
Ag(111)



L. Casalis, M. F. Danisman,B. Nickel,G. Bracco,
T. Toccoli, S. Iannotta, and G. Scoles, PRL 90 (2003) 206101

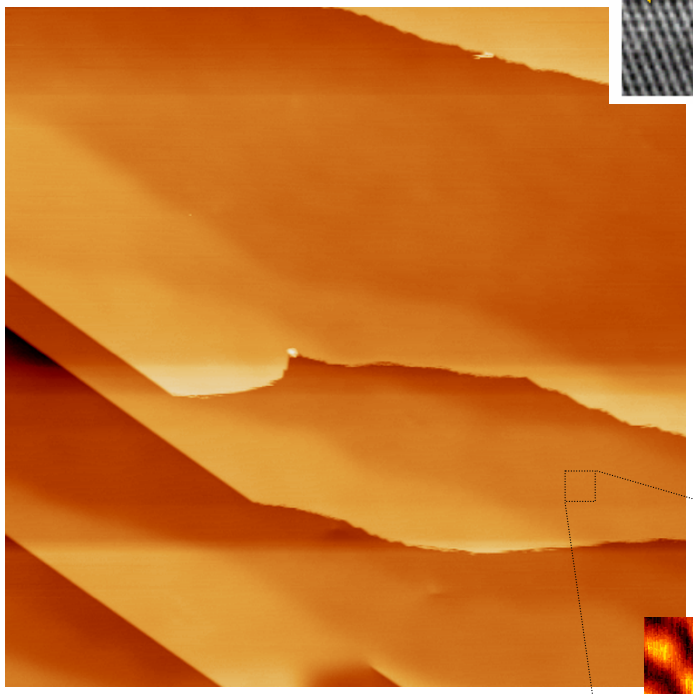
Bi(001)/Si(111) template for pentacene growth

30 BL Bi(001) on Si(111)
As deposited at RT

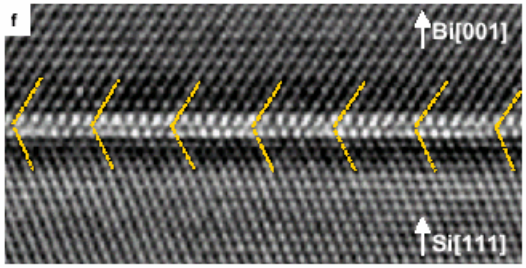


2000 Å x 2000 Å, -1.7V, 20pA

30 BL Bi(001) on Si(111)
Annealed at ~90 °C

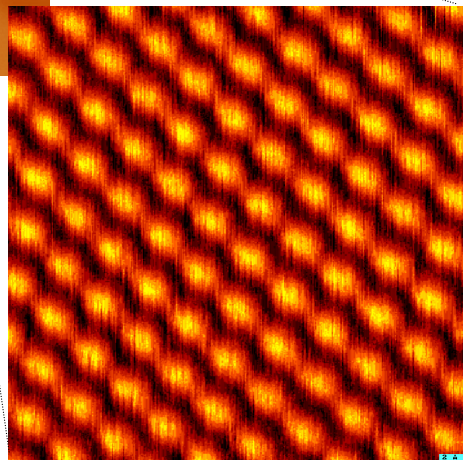


2000 Å x 2000 Å, -1.7V, 20pA



T.Nagao et al.

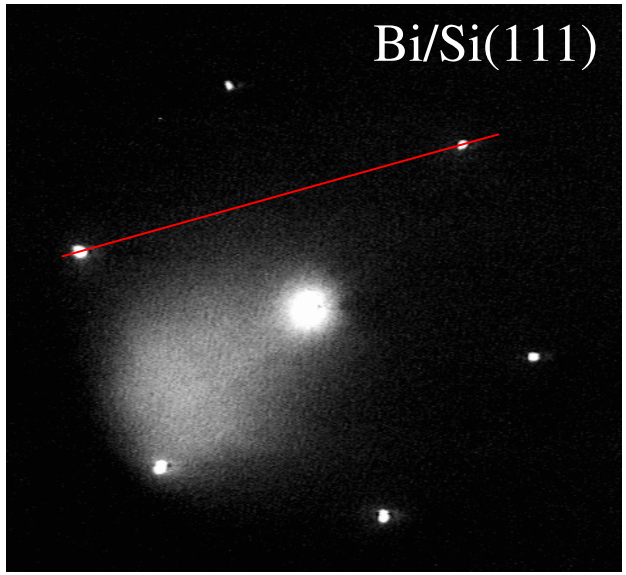
Bi(001)

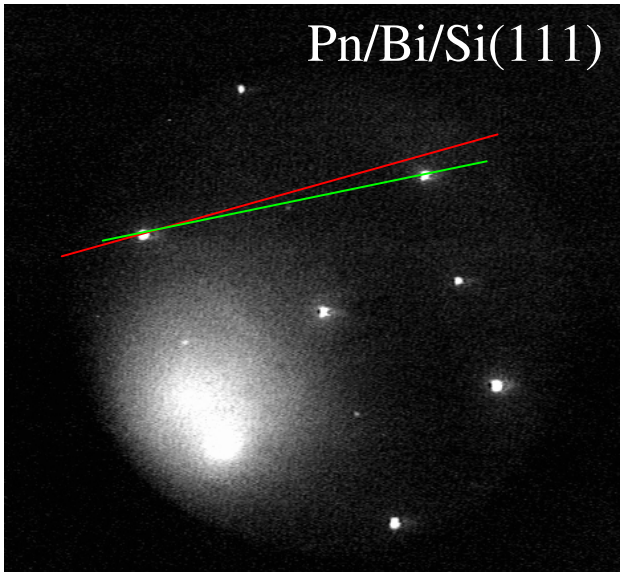


40 Å x 40 Å, -0.04V, 300pA

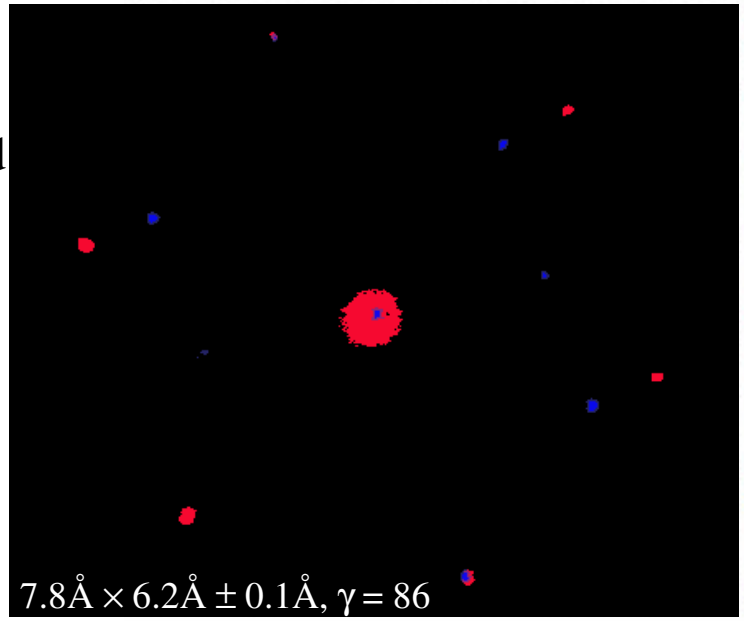
Annealing leads to decreasing of the step density on Bi(001) surface, making it potential template for organic thin film growth

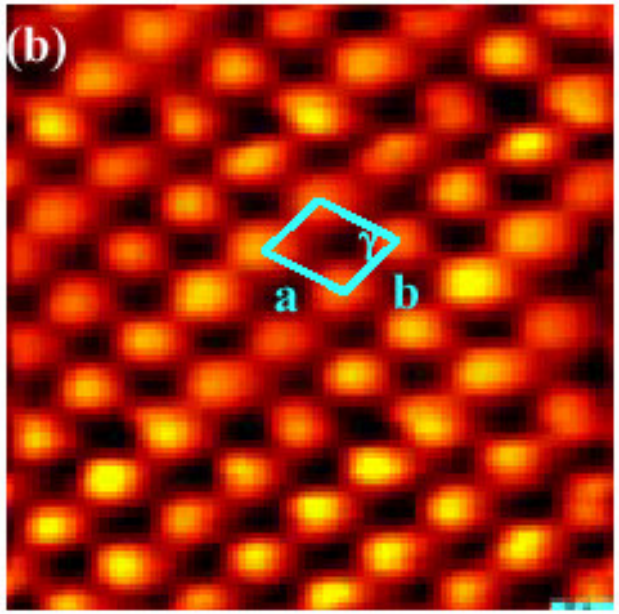
Structure of pentacene on Bi





Bi epitaxial on Si
Pentacene epitaxial on Bi
Strong and highly ordered diffraction
Pentacene stands up

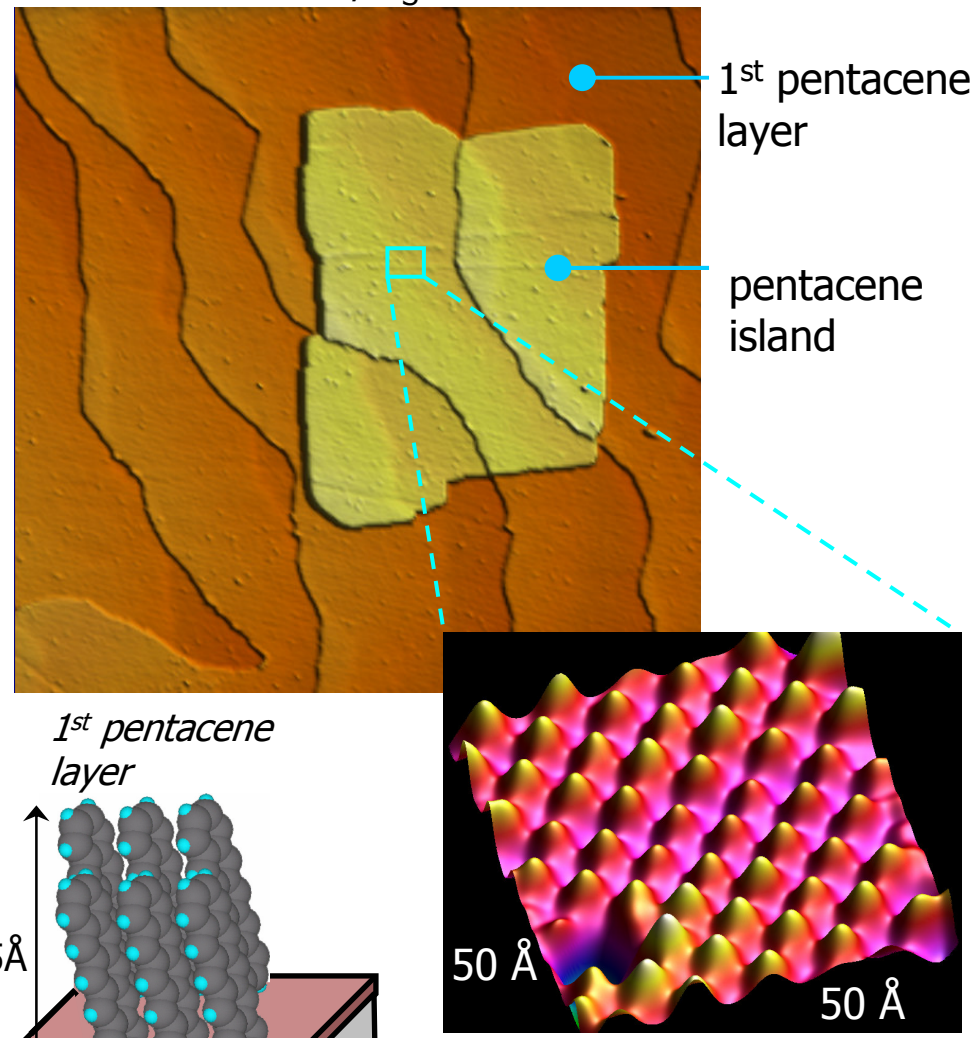


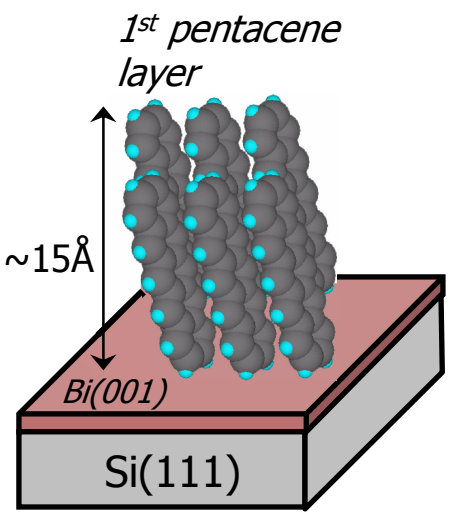


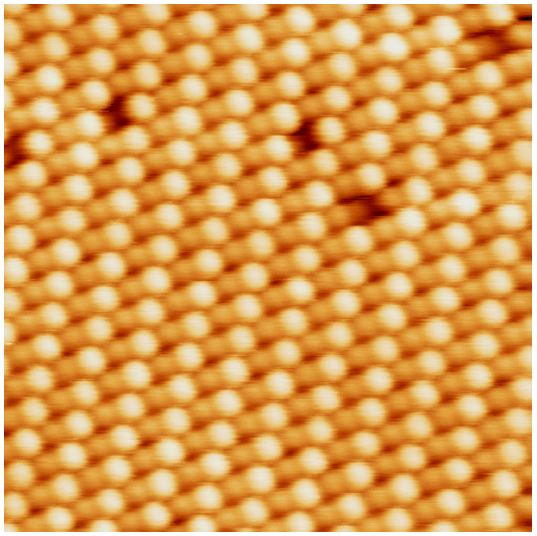
G.E. Thayer, J. Sadowski, R.M. Tromp, unpublished

Pentacene growth on Bi(001)/Si(111)

500 nm × 500 nm, V_S = -2.0V



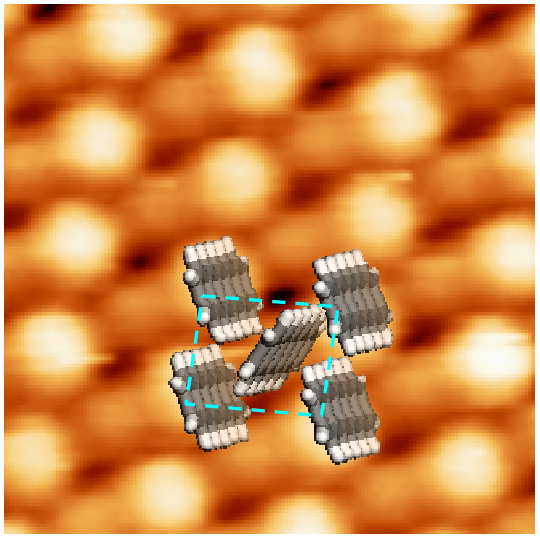


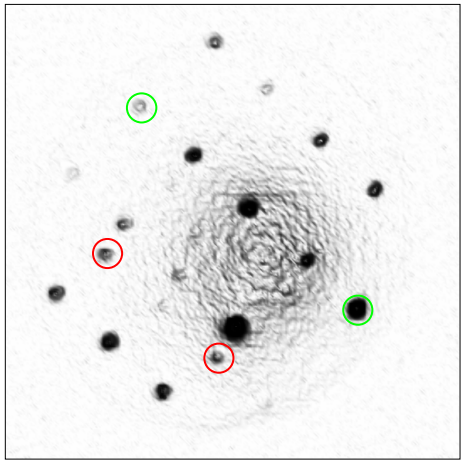


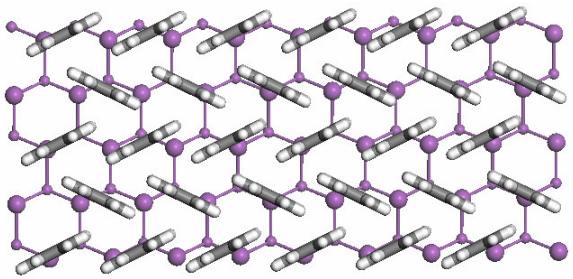
In-plane lattice parameters:
a = 7.8 Å ± 0.2 Å
b = 6.9 Å ± 0.2 Å
γ= 88° ± 0.5°

Good agreement with bulk lattice.

Pentacene on Bi structure

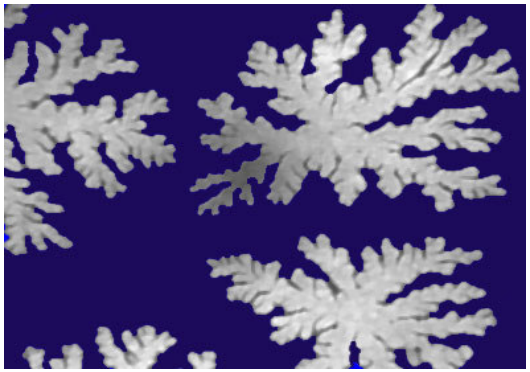






Pentacene molecules align with major crystal axis – commensurate in one direction, incommensurate in the other.

Conclusions

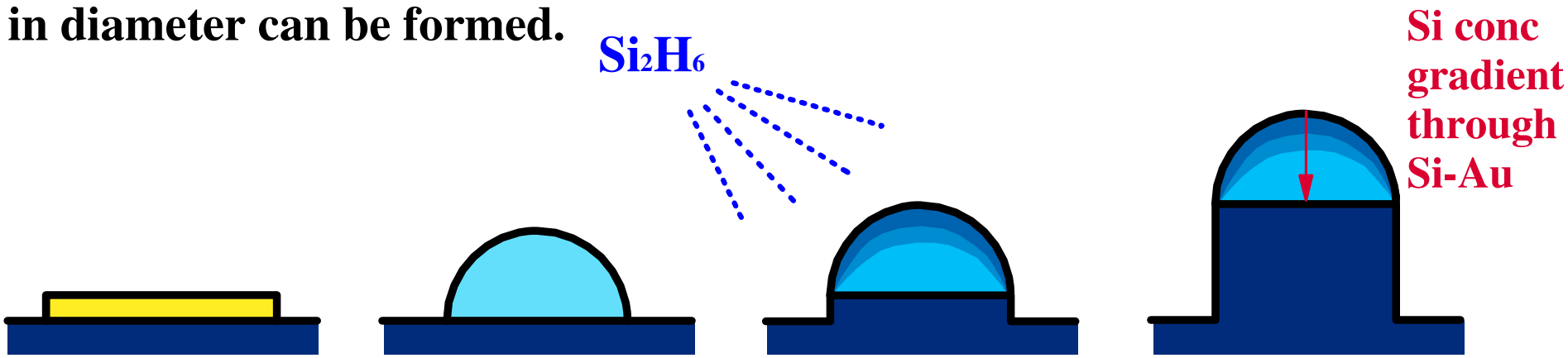


- Growth mode of pentacene is controlled by the nature of the substrate surface
- Molecule can react covalently with clean Si
- Molecular orientation is determined by a competition of molecule-molecule vs molecule-substrate interactions.
- Molecule stands up on insulating, semiconducting, or semimetallic surfaces, but has planar orientation on metallic surfaces.
- Self assembled organic monolayers provide a ‘tunable’ interface between pentacene and reactive substrates
- Pentacene epitaxy seen on semiconductors and metals
- PEEM/LEEM provide real-time view of growth of delicate materials

IBM

Si nanowires: The VLS process for Si/Au

The VLS process has been examined in most detail for Si wire growth catalysed by Au. The process relies on a concentration gradient set up in a liquid eutectic by the presence of a crystalline Si surface. Wires below 10nm in diameter can be formed.

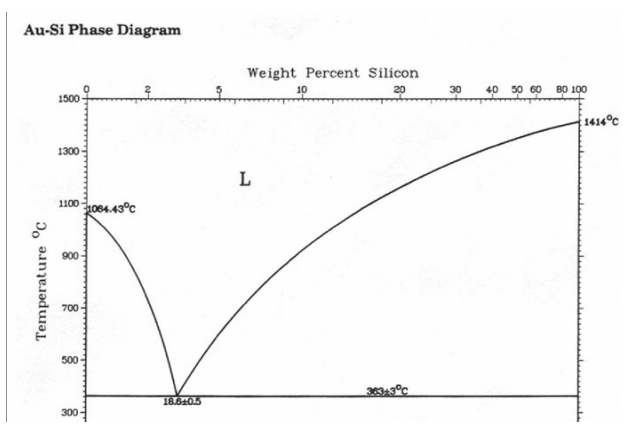


Deposit Au on HF-dipped Si

Heat above 370$_o$C to form Si-Au eutectic

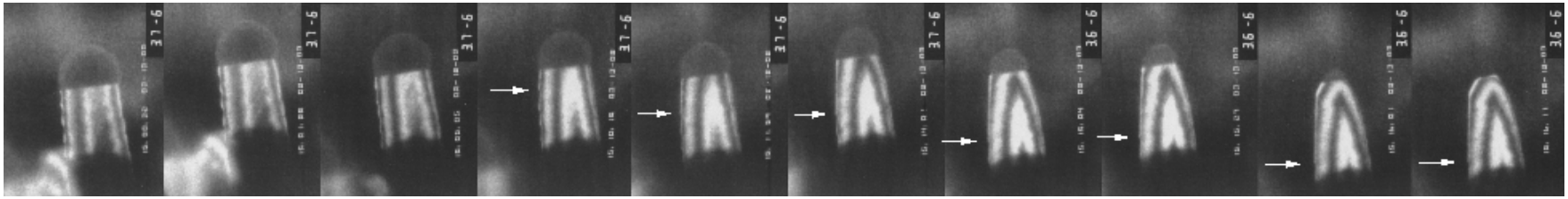
Expose to disilane gas

Continue growth



A strange observation

Au catalyzed growth of Si nanowire: Wire tapers off as Au is consumed in the reaction



- *In situ* TEM measurements show that the Au catalyst can become unstable during growth, leading to a sudden tapering and termination of the nanowire.

- What causes this apparent instability?

  – Possibly some change taking place at the surface of the nanowire?

  – Our goal: Investigate the stability of Au films on Si(111) and Si(100).

Grow nanowires in a well-characterized environment

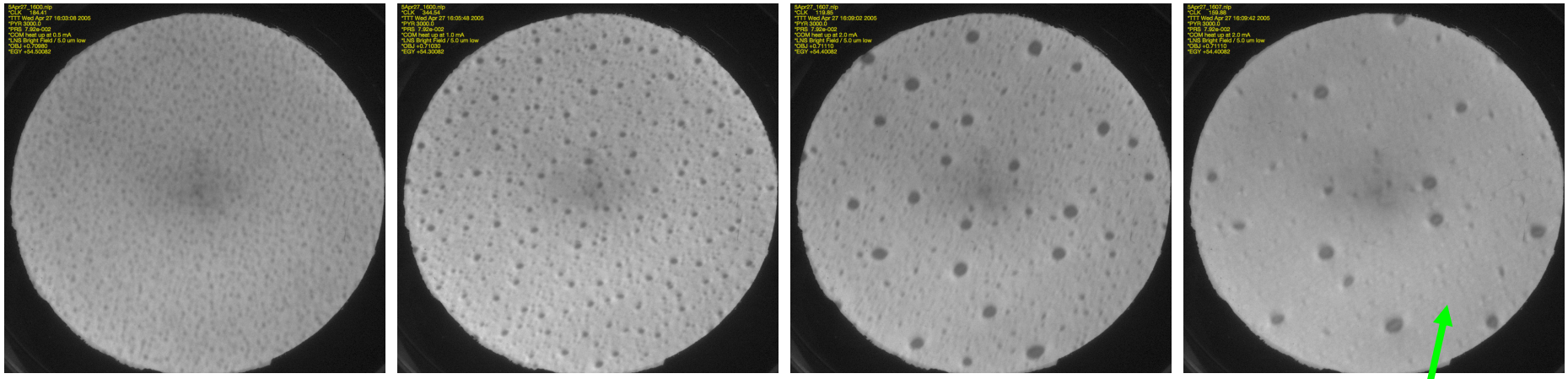
- Clean ultra-flat Si(111) in UHV by flashing to ~1200 C
  - Image a 10-20 um wide step-free terrace
- Grow ~2.5 ML of Au via MBE at room temperature
  - Underlying 7x7 domain structure is intact
- Anneal in UHV to ~500 C. Au layer partially dewets
  - Au droplets on a $\sqrt{3}x\sqrt{3}$ Au wetting layer
- Expose surface to disilane (20% in He) p = $5x10^{-5}$ to $5x10^{-4}$ Torr
- Image surface post-growth using LEED, LEEM, PEEM
- *Ex situ* SEM, AFM

Two key results

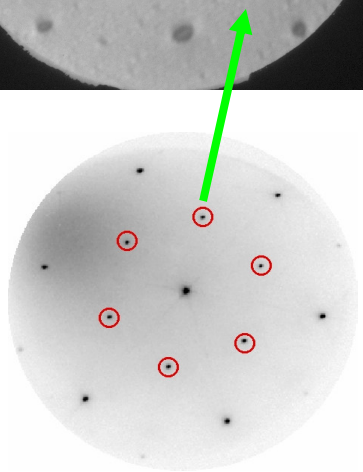
- Au catalysts coarsen <u>during</u> VLS growth
  - Evolution of catalyst size influences the wire profile
- Nanowire growth <u>consumes</u> Au
  - Both the nanowires <u>and</u> substrates are covered by Au.
  - There is consequently a fundamental limit to the length of a nanowire

Au catalysts coarsen at ~500 C

- Density decreases while average size increases with time

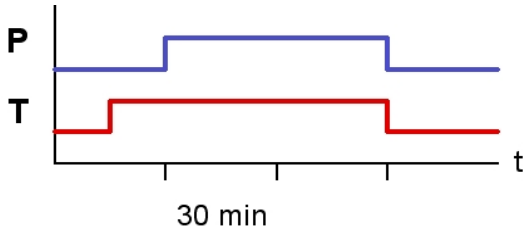


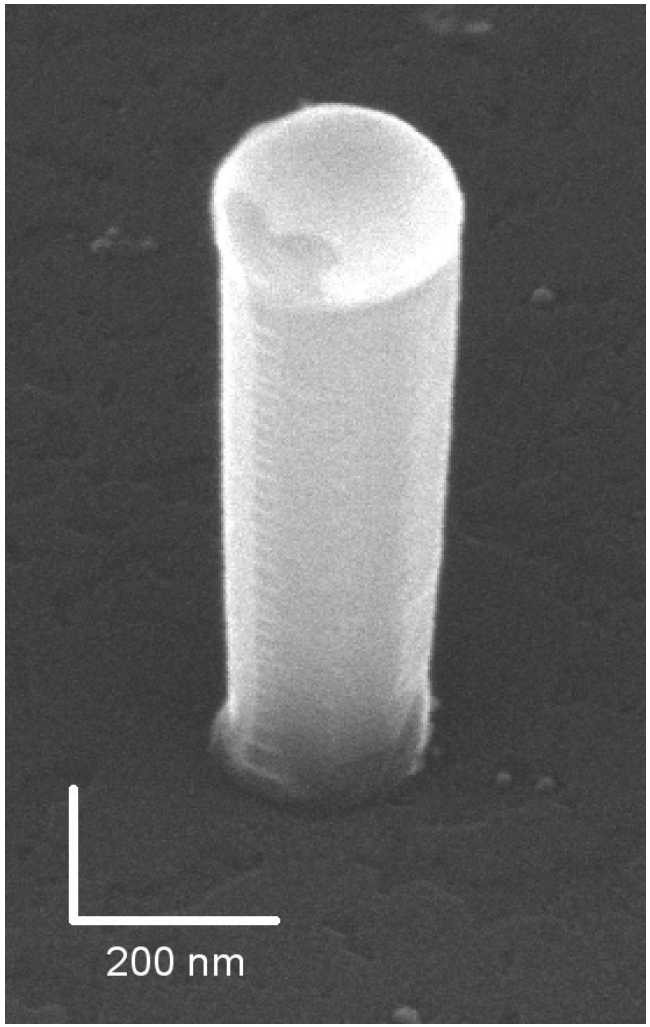
5 um field of view, time →

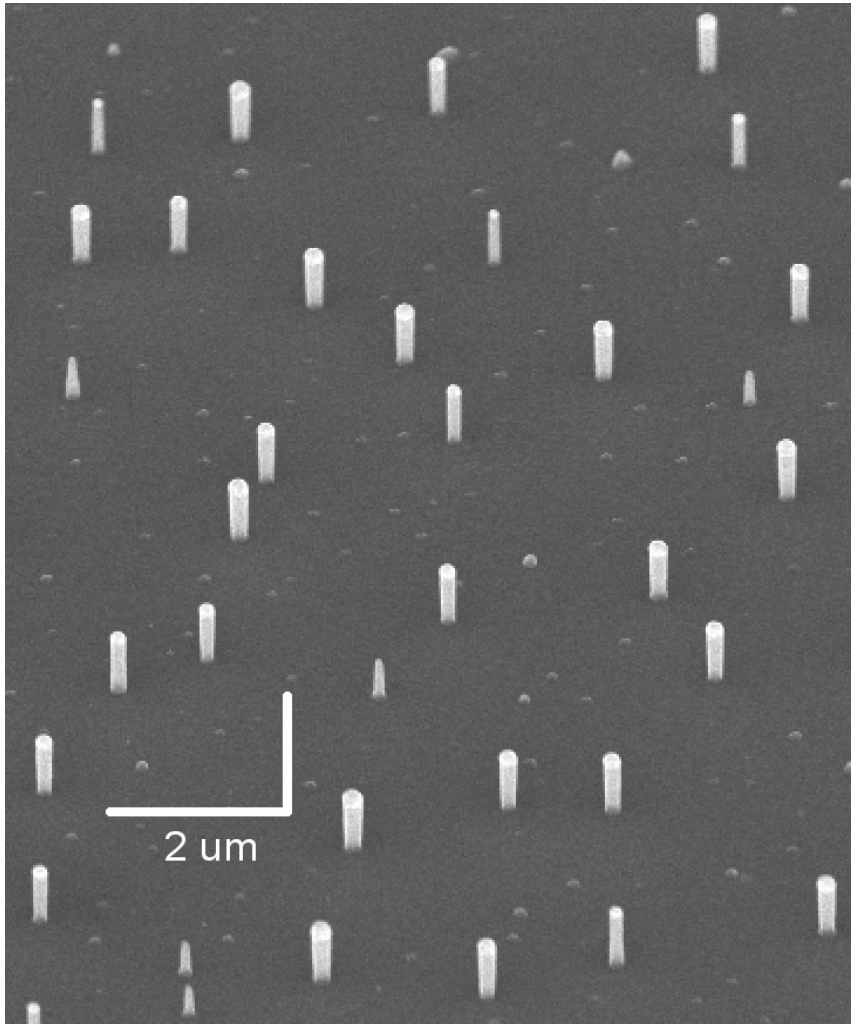


Grow nanowires in the LEEM

- **Anneal 2.5 ML Au film in LEEM to form catalyst droplets.**
- **Expose to $5x10^{-5}$ Torr disilane for one hour at ~500 C.**



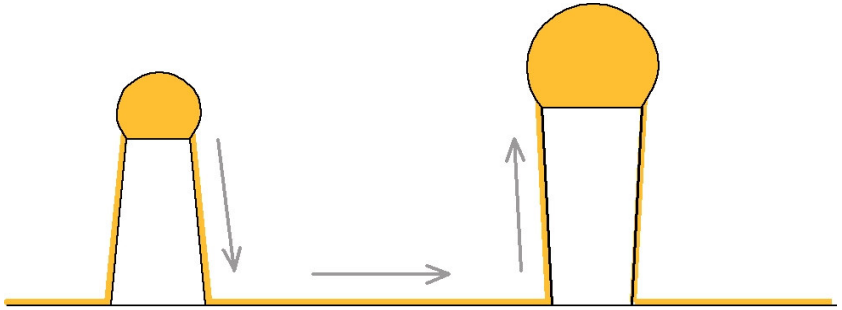




Is this coarsening *during* nanowire growth?

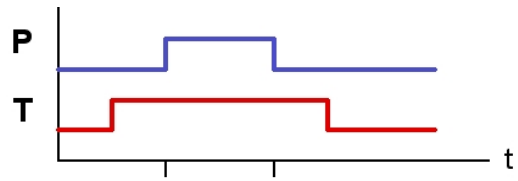
- Catalysts clearly coarsen at ~500 C before growth

- If Au decorates the wires, coarsening should continue during growth

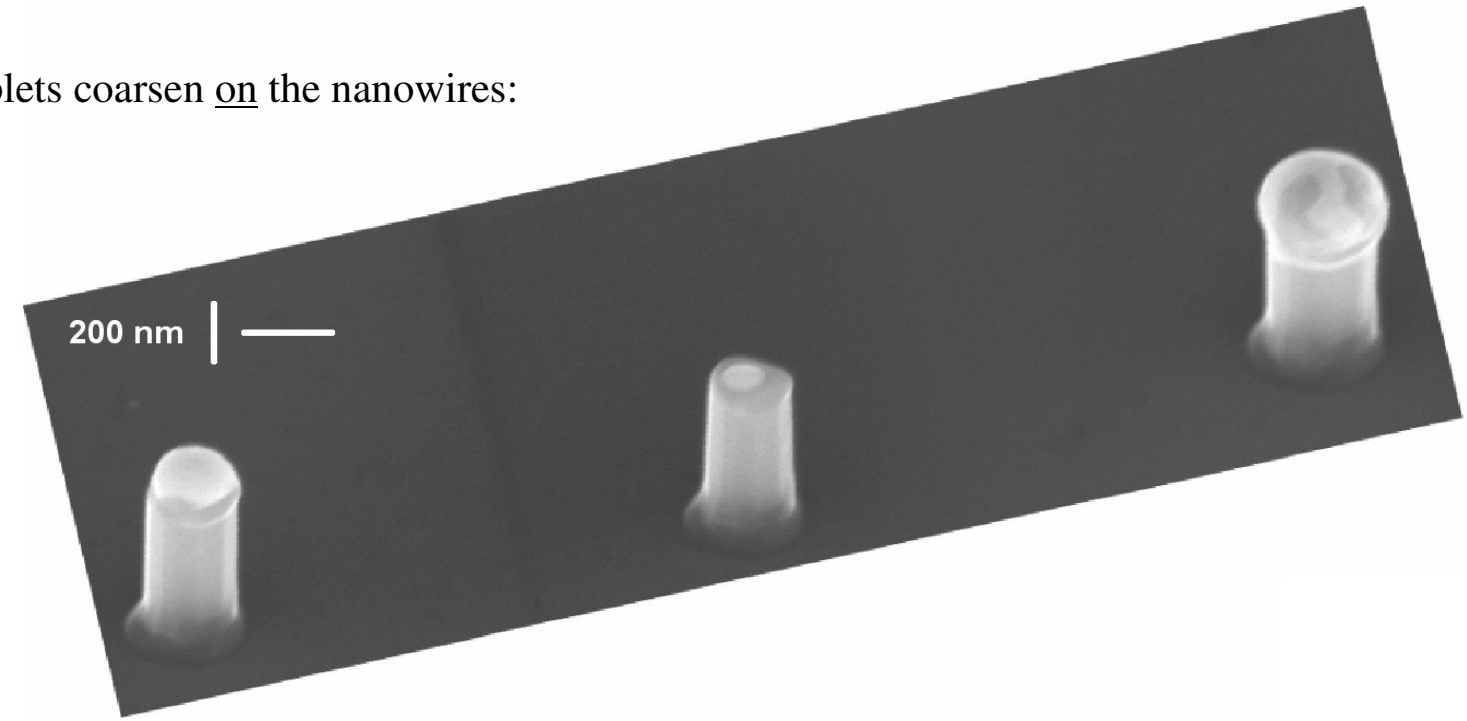


Test: continue annealing <u>after</u> growth

- Preheat to form catalyst particles
- Grow at 5×10^{-5} Torr disilane, 500 C
- Heat for 30 min. following growth

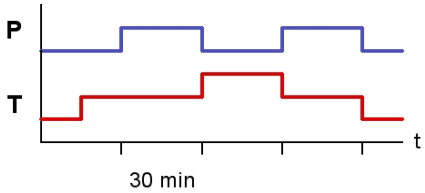


  – Au droplets coarsen <u>on</u> the nanowires:

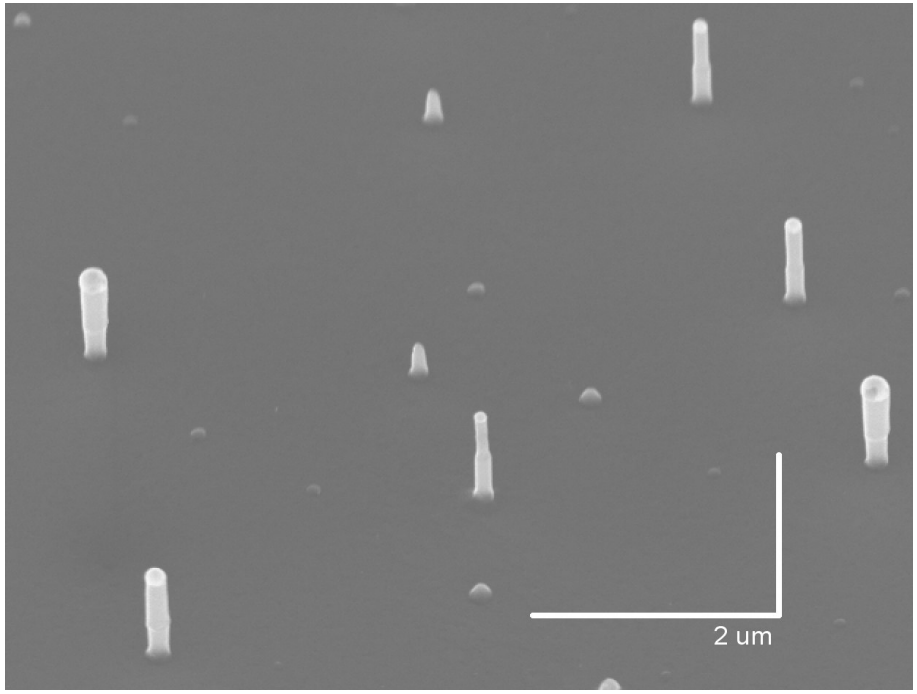


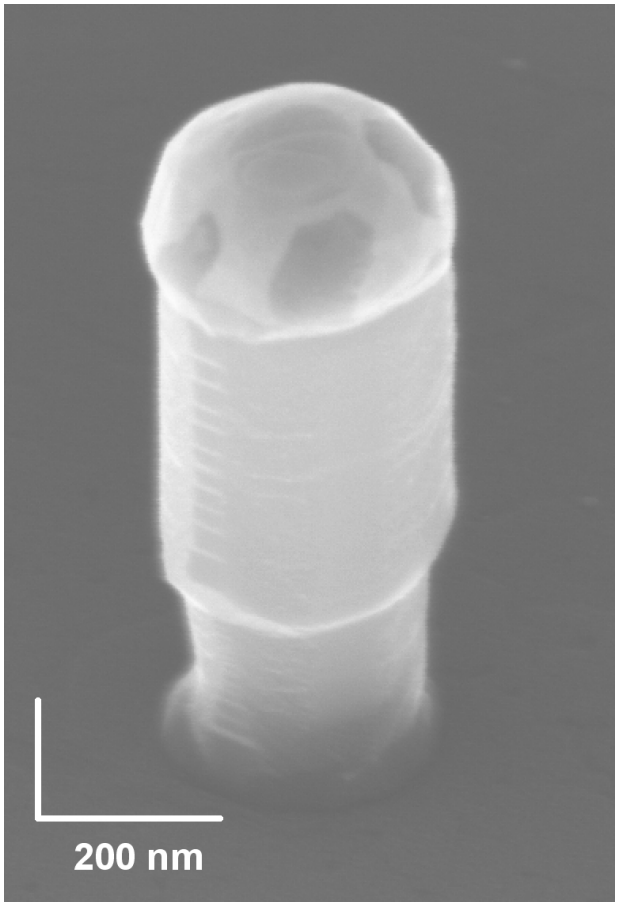
SEM: 042805_12

Exploit coarsening to ‘engineer’ nanowire profile



- Grow for 30 min. at 5×10^{-5} Torr disilane, 500 C
- Anneal at higher temperature (~600 C) with no disilane
- Resume growth after coarsening





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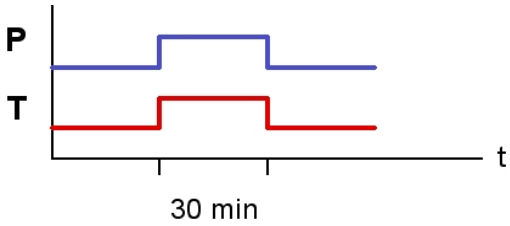
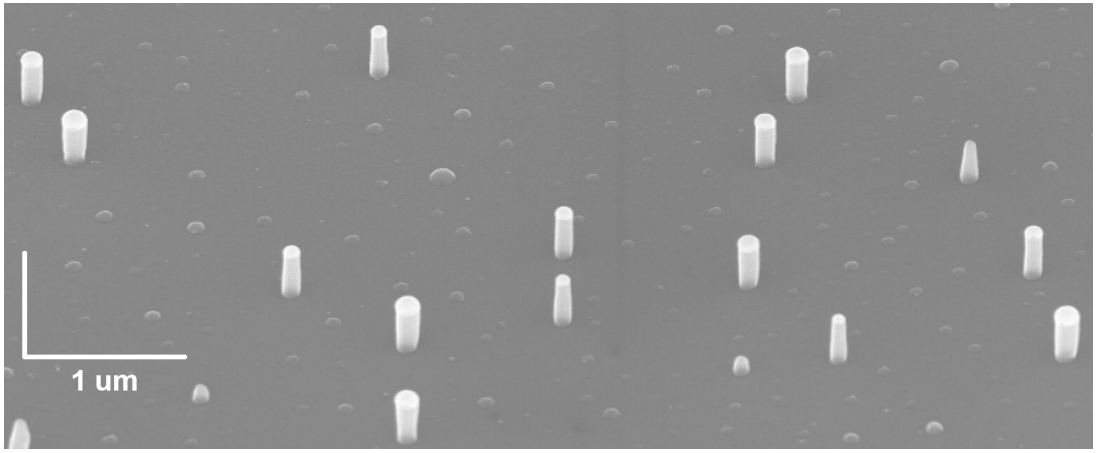
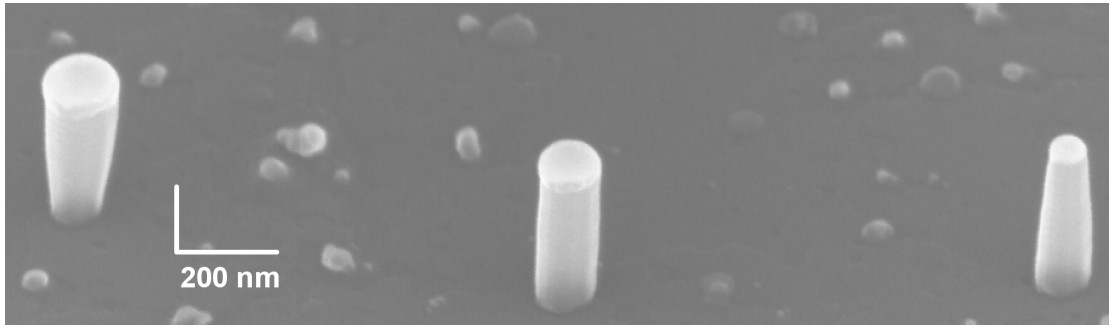
Exaggerate coarsening effects: no pre-heating

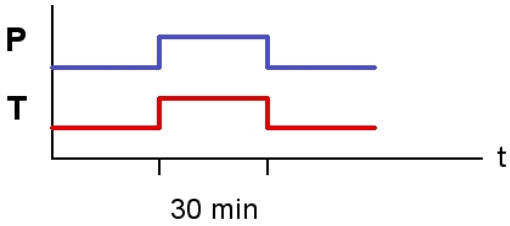


- Anneal 2.5 ML Au film in disilane background (p = 5×10^{-5} Torr)
- No straight sidewalls!

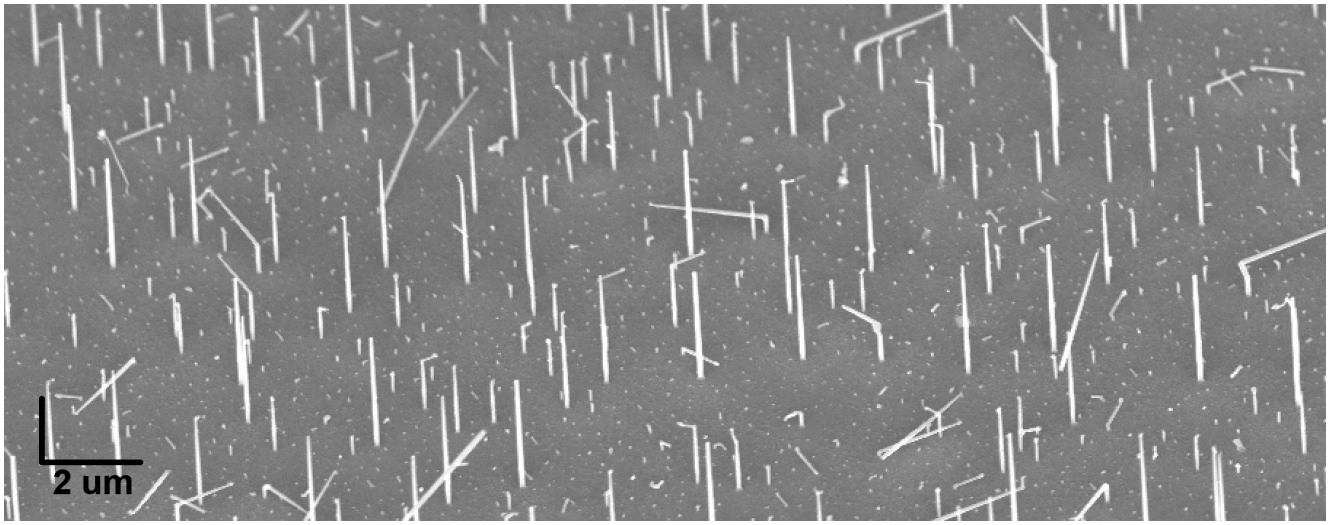




Towards reality: 10x higher pressure

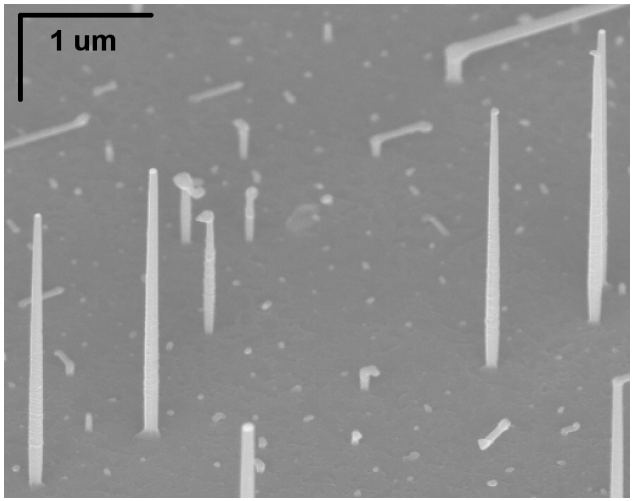


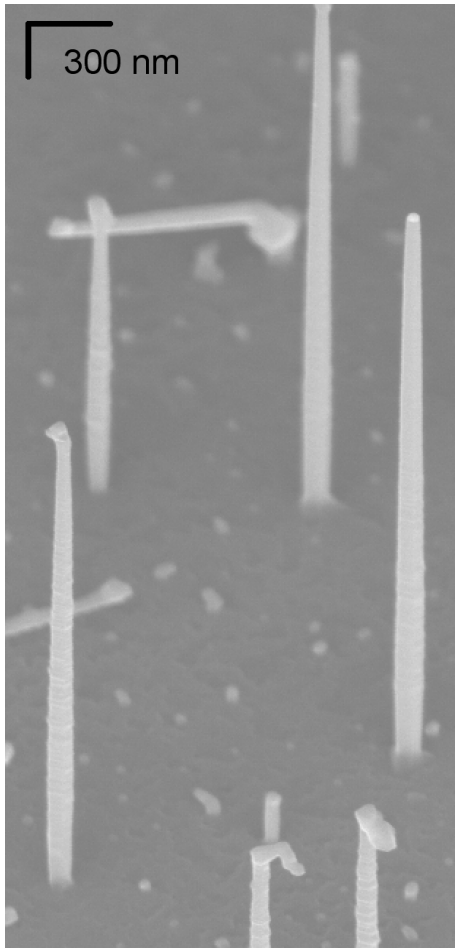
- Can we "beat" the coarsening with faster growth?
- All nanowires taper – *all* Au catalysts show decay



Coarsening then tapering…

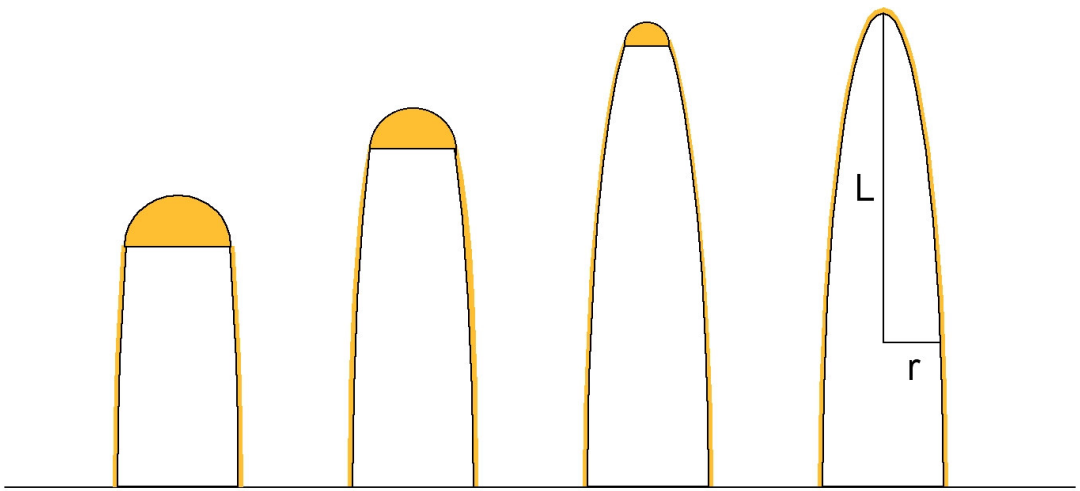
- Why tapering?
- Why are there no large catalysts?
- Where has all the Au gone??





Au is *consumed* during growth

- Simple model: As the nanowire grows, Au is taken from the (hemispherical) catalyst to coat the side wall.



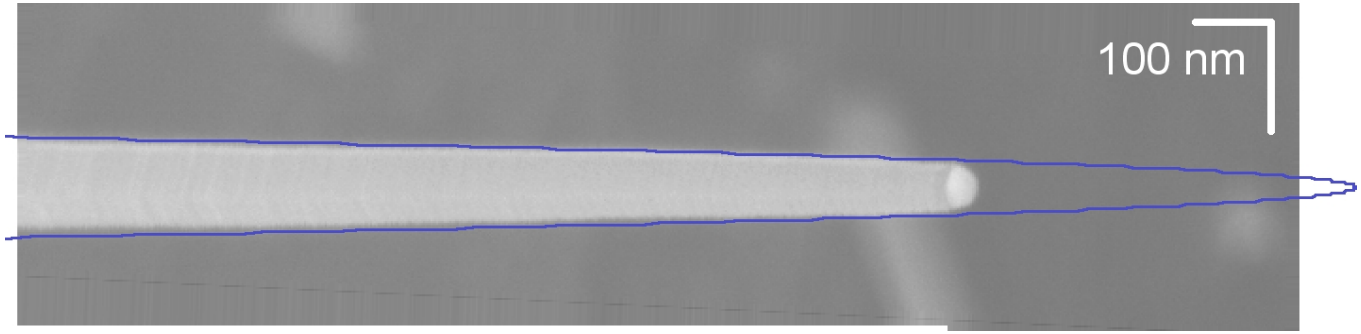
$$r = \sqrt{\frac{2a\,L}{\kappa}}$$

$$a^3 = \text{atomic volume}$$

$$a = 0.26 \text{ nm}$$

$$\kappa = \text{surface density } \times a^2$$

Expect k >= 1



Conclusions

- At low-pressure, VLS nanowire growth on clean Si(111) is fundamentally limited
  - Coarsening leads to tapered nanowires
  - Au catalysts are eventually consumed by the sidewalls of the nanowires.
  - There is a maximum wire length.
  - Small amounts of oxygen have a large effect on nanowire growth and enable growth of long, untapered nanowires.

Thanks to Frances Ross, Suneel Kodambaka, Emanuel Tutuc, and Mark Reuter

Cu-Pd surface alloy formation

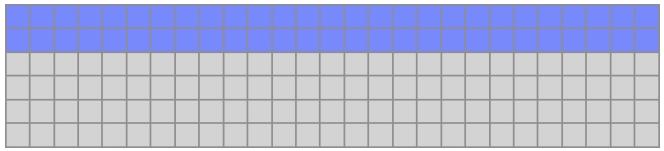
- Experiments: Jim Hannon and Gary Kellogg
  - ELMITEC LEEM III at Sandia National Labs

- Calculations: Jiebing Sun and Karsten Pohl
  - Department of Physics, University of New Hampshire

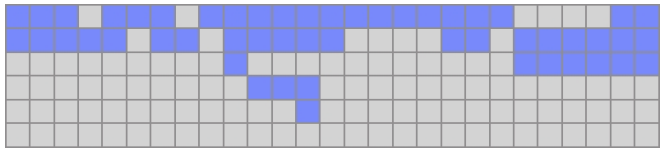
A fundamental issue in thin-film growth

- It is well known that thin films can be <u>heterogeneous</u>, but determining the atomic-scale mechanisms responsible for inhomogeneity is difficult.
  - Thin film heterogeneity is obviously a key issue in microelectronics.

You want this….



…but you get this. Why?



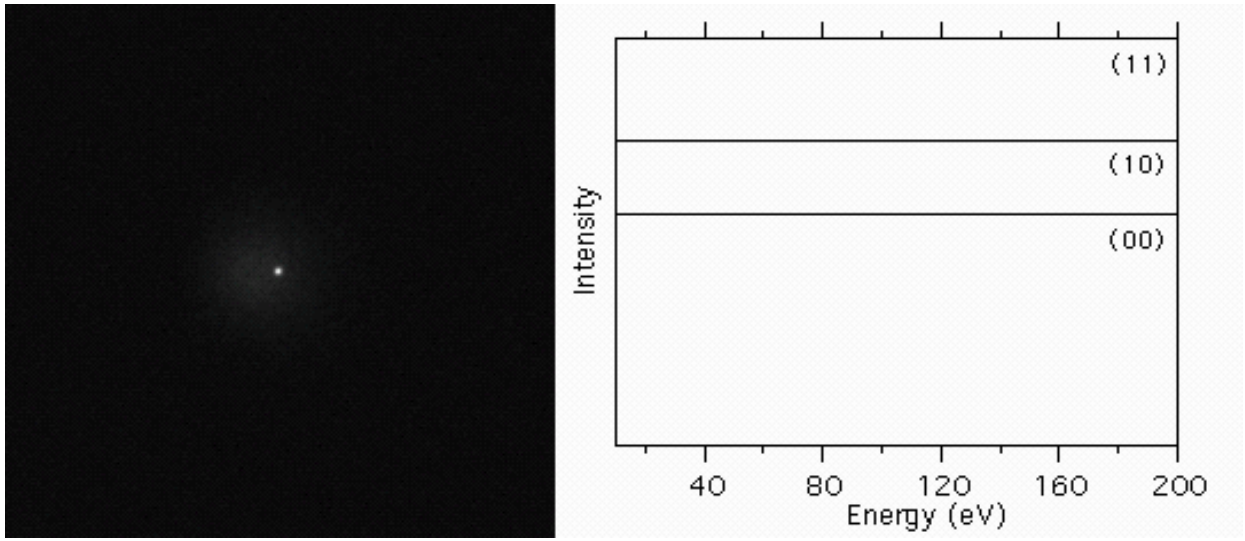
- To understand the limiting kinetics, you need to <u>measure</u> how heterogeneity develops in 3D with good time resolution
- Example : Pd on Cu(001)

Conventional LEED-IV with a LEEM

- Conventional LEED is routinely done with LEEM
  - Image the diffraction plane instead of the image plane (i.e. no spatial resolution)

- "IV" analysis can also be done, but there are important differences:
  - (00) beam can be analyzed
  - Typically the electron kinetic energies are lower in LEEM
  - Sample a smaller fraction of *k*-space.
  -

Clean Cu(001)

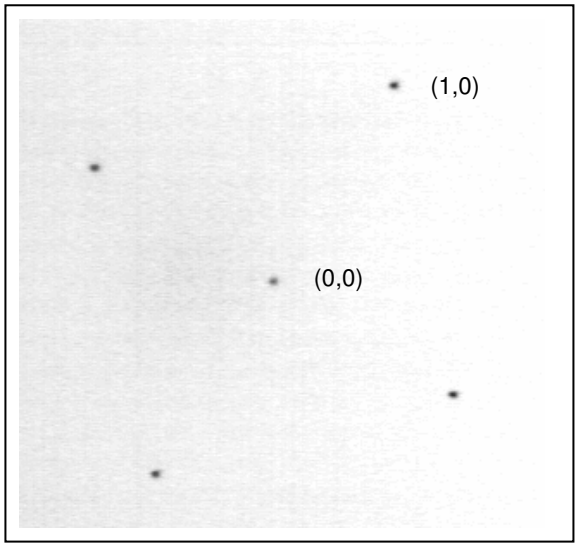


Diffracted intensity for the (00), (10), and (11) diffraction peaks from clean Cu(001) at 40 C.

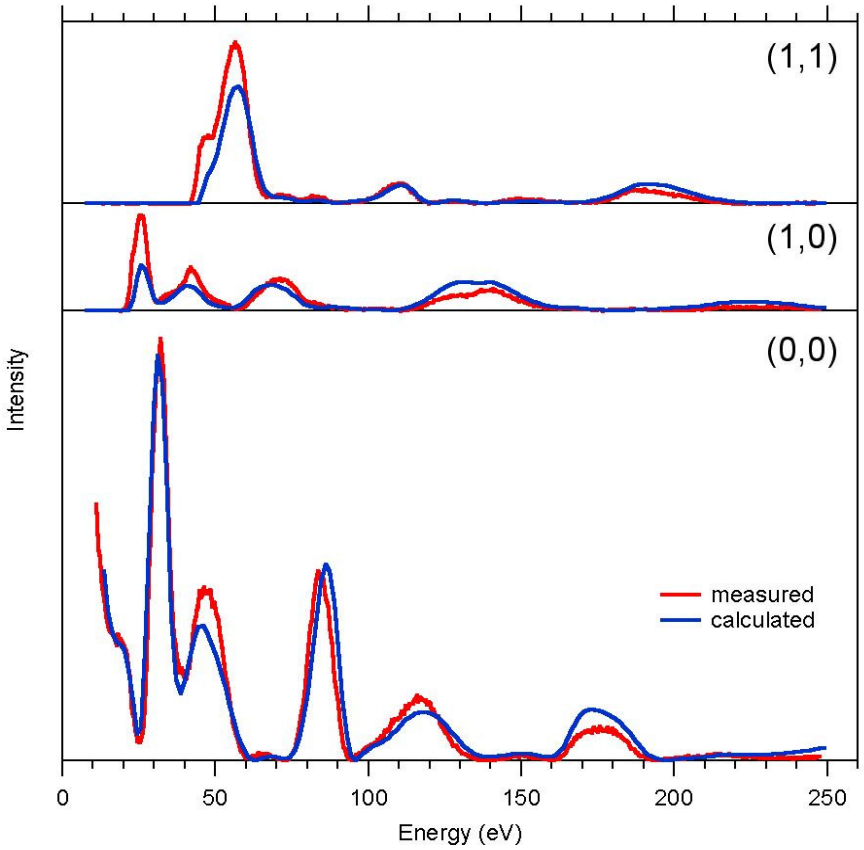
LEED: 120704B

LEED-IV of Clean Cu(001)

- 200 °C
- R = 0.049
- d_{12} = 1.79 A (-0.8 %)
- d_{23} = 1.83 A (+1.1 %)
  (bulk spacing 1.806 A)



Clean Cu(001) 200 °C, 28 eV

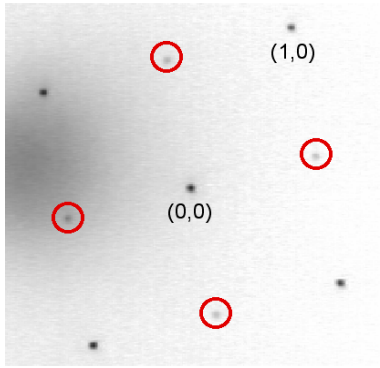


120704 data

Pd growth on Cu

- Clearly heterogeneous, even when grown at 200 C with a very low flux
  - (also despite sharp 2x2 diffraction pattern)

- What is the kinetic limitation that causes this?

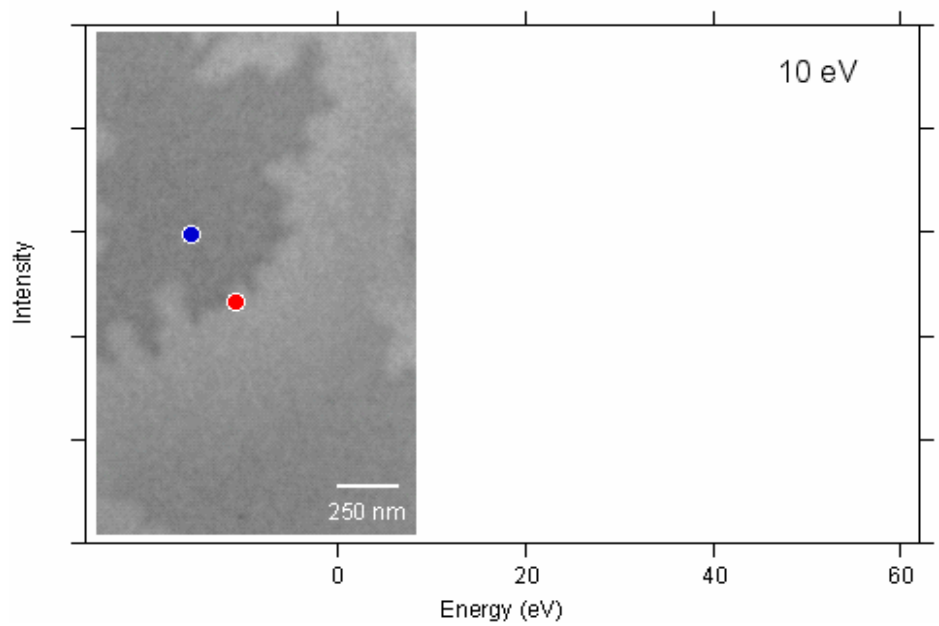


8 um Field of View, 13.1 eV, 0.6 ML @ 2.5 ML/hr Pd, 200 C

Image: 172/14450F750
LEED: 172/15446F164

Spatially-resolved "I-V" profiles – LEEM I-V

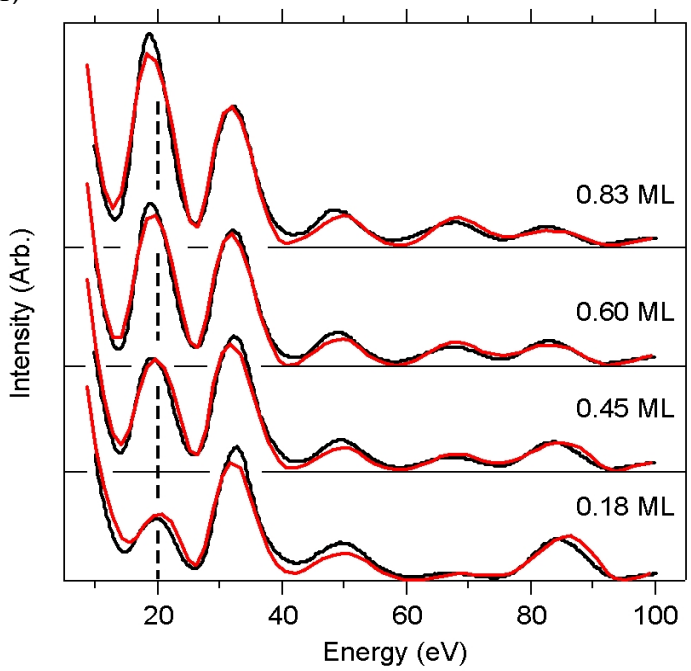
- Late stage of growth (after deposition of ~0.85 ML of Pd)
- Ramp electron energy 5 – 100 eV.
- Do it over and over again during deposition (time evolution)

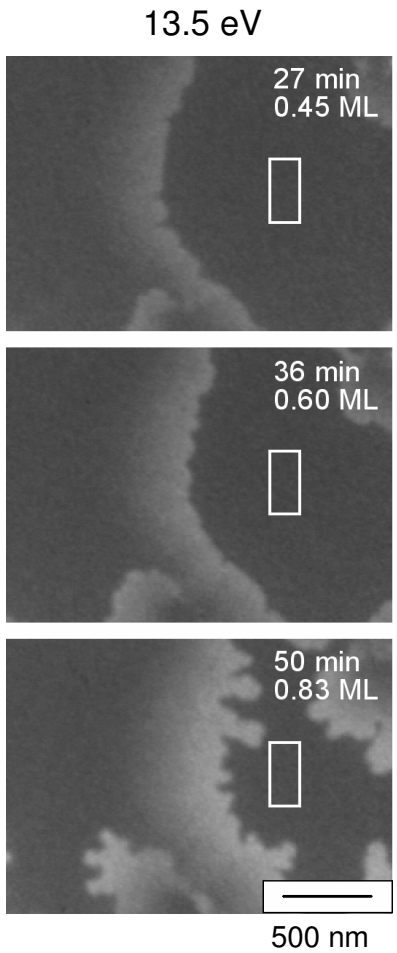


1105_R

Simplest analysis: the terrace far from a step

- Intensity is homogeneous
- Peak at 20 eV grows with time (Pd coverage)
- Structural parameters
  - Pd concentration in 1st three layers
  - Interlayer spacing
  - Two c(2x2) sublattices, rippling
- Calculation favors 2x2 cell
  - (in agreement with prev. work)

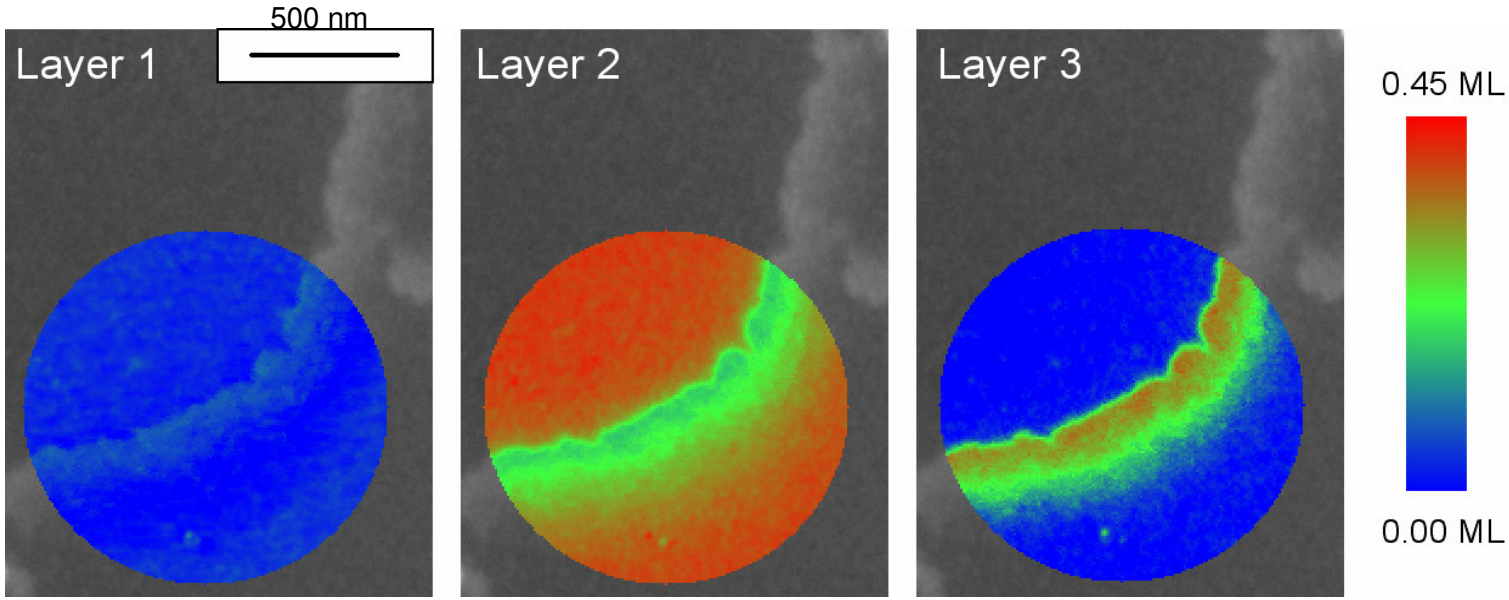




1105_G,K,N,R

Quantitative pixel-by-pixel IV analysis: layer-by-layer composition maps

- Analyze the IV curves from individual 17,000+ individual pixels (9 nm x 9 nm)
- Very little scatter – statistical errors are small



LEEM-IV conclusions

- Pd/Cu(001) is heterogeneous even when grown at high T with a low flux
- Step overgrowth mechanism is responsible
  - Fundamental differences between surface and bulk mass transport
- Pd in first two layers is mobile and equilibrated
- Correlation in Pd coverage gives insight into the energetics
  - Pd-Cu NN bonds are favored over Cu-Cu or Pd-Pd by 25 meV

- We can measure atomic-scale composition profiles – LEEM-IV works.

Summary

- LEEM is applicable in many different materials systems, including delicate organic materials
- In-situ real-time imaging capability turns the microscope from a post-mortem instrument to a materials lab in itself
- LEEM provides quantitative data, both in image and diffraction
- Magnetic information available with spin polarized gun

- Combination with PEEM provides additional analytical and spectroscopic information – much room for instrument improvement
- Aberration correction will improve resolution to ~ 1 nm