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Heteronucleation of Zinc Oxide Nanocrystals

Julia W. P. Hsu

T. L. Sounart, Z. R. Tian,
M. Clift, L. Brewer, J. Floro, J. Michael,
N. C. Simmons, C. M. Matzke, B. McKenzie,
J. A. Voigt, & J. Liu

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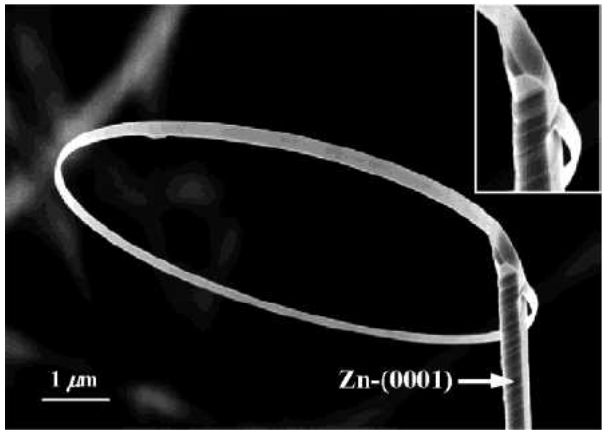
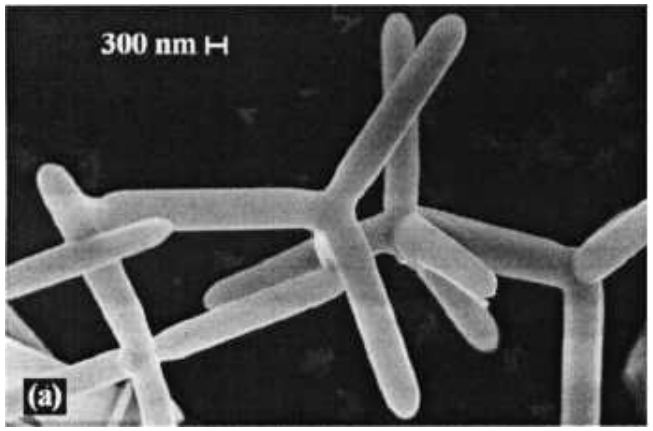
Motivation

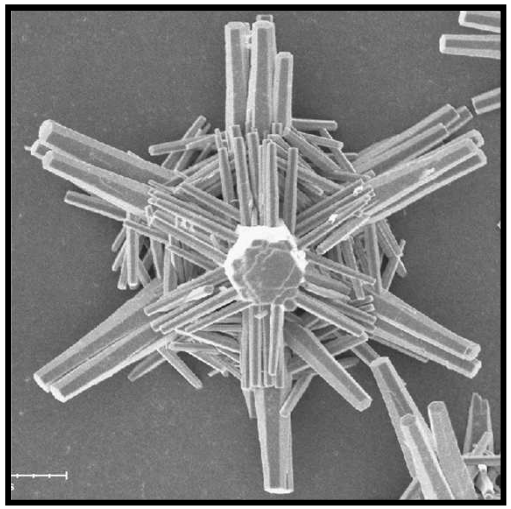
Complex ZnO Nanostructures



Nanobelt
Georgia Tech



Tetrapods
U. Hong Kong



Hierarchical nanostructures, Sandia

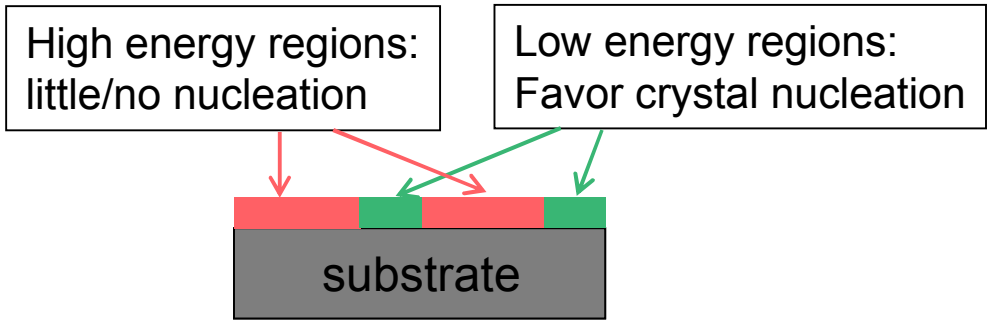
- ZnO: wide bandgap semiconductor, piezoelectric, transparent conductor, spintronics
- Explosion in nanomaterials synthesis
- To make these new materials useful:
  (Directed) Assembly -- placement, density, orientation
- Conventional 2D lithography inadequate

Experimental Approach

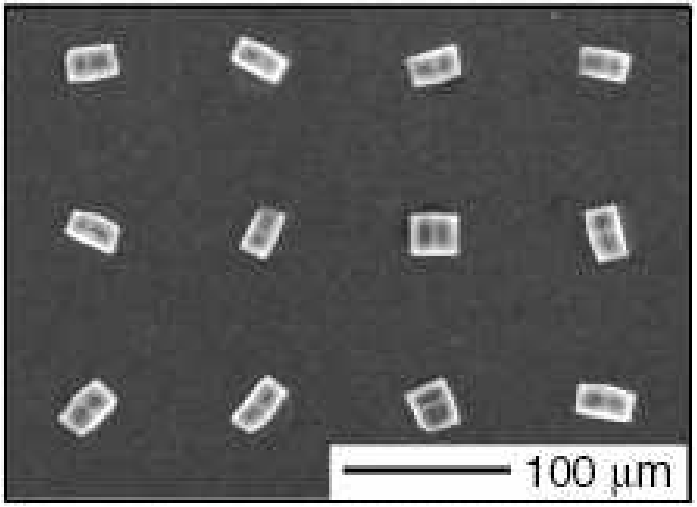
- Solution growth: low temperature (organic template/modifiers possible), environmentally benign, large area uniformity

+

- Soft lithography (microcontact printing): to *chemically* modify the surface and create regions on surface where the nucleation energy is different



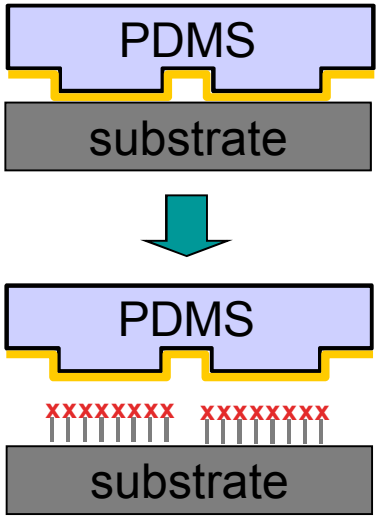
calcite



Aizenberg, Nature, 1999

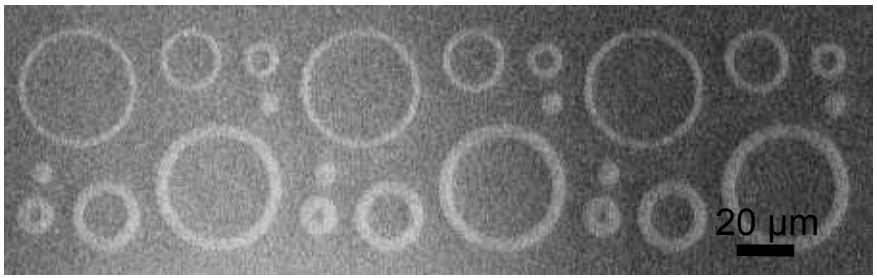
- "Bio-inspired": use organic template to direct inorganic materials growth
- Extend to ZnO: a technologically important material

Microcontact Printing



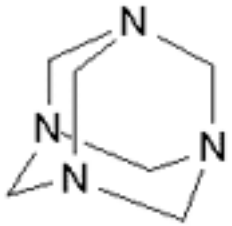
$HSC_{10}H_{20}COOH$

$HSC_{15}H_{30}CH_3$



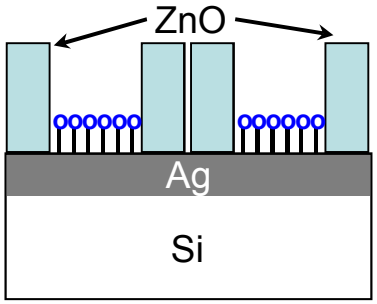
Solution Growth

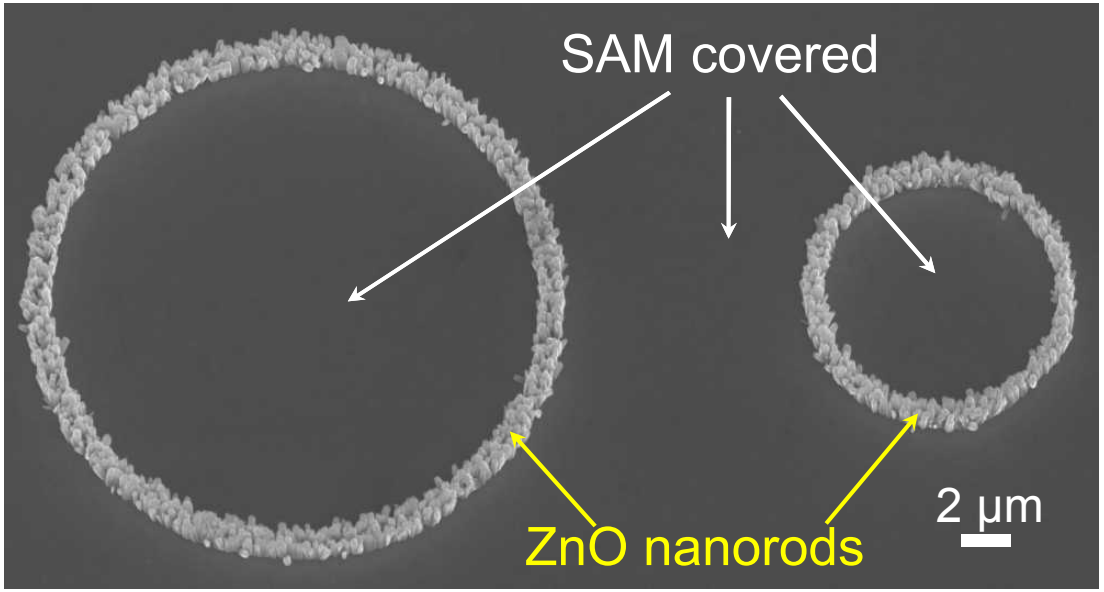
- Dilute $Zn(NO_3)_2$ + HMT

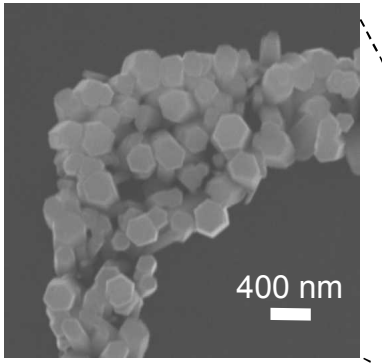


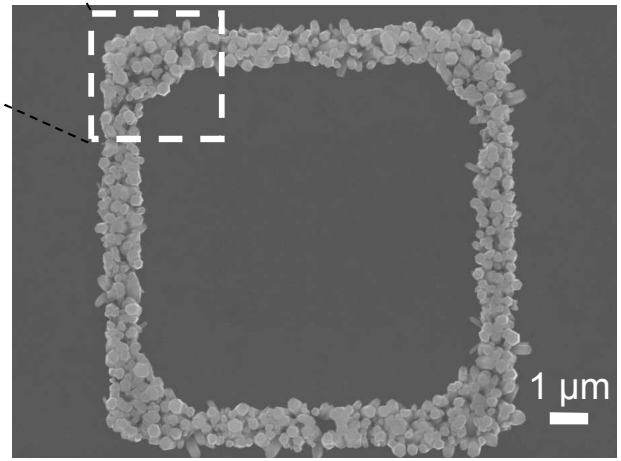
- T = 55 - 65 ° C
- Time = 2 to 6 hrs
- ZnO growth mediated by HMT degradation
- Demonstrate control in
  - spatial placement
  - crystal orientation
  - and nucleation density

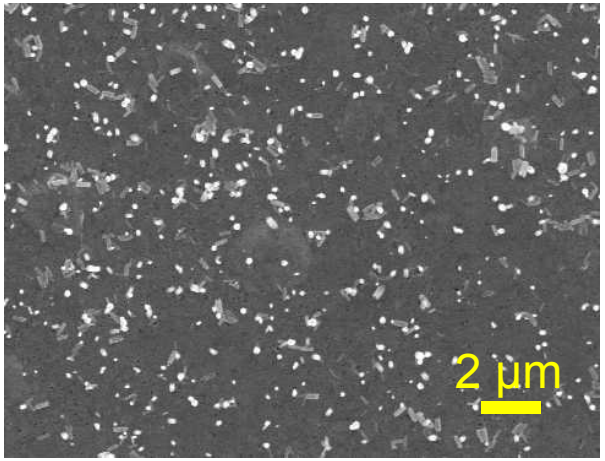
Selective ZnO Growth on Ag











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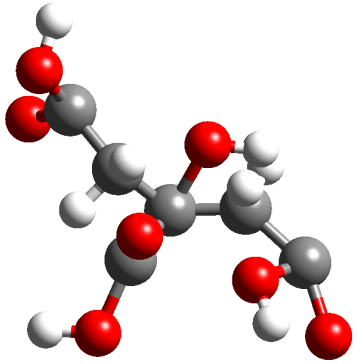
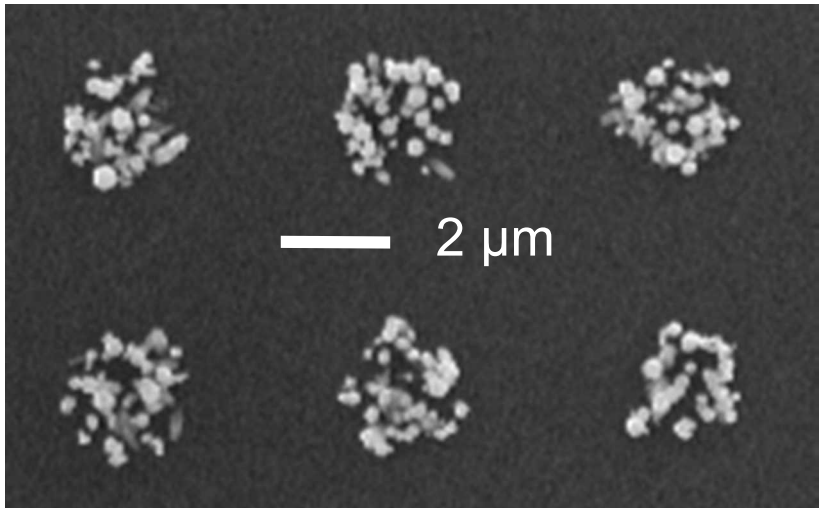
Nucleation Density Control: Growth Modifier

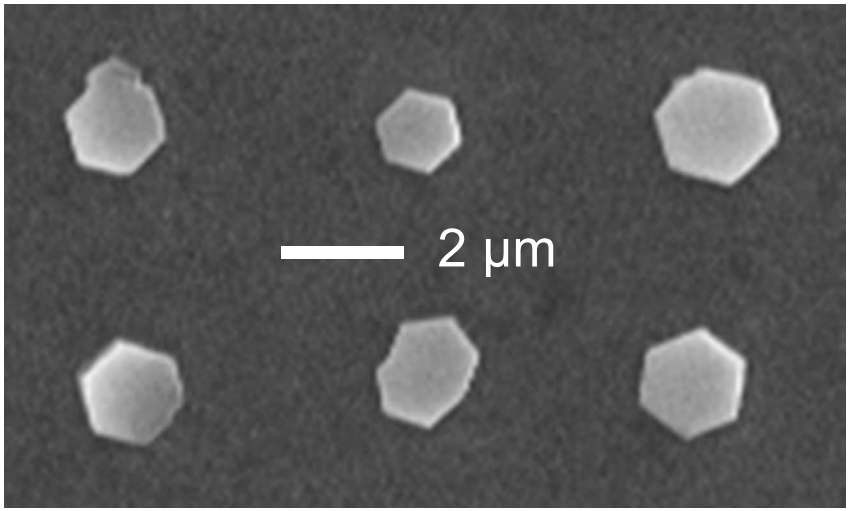


$(COO)_3COOH(CH_2)_6$ (-3)

Citrate inhibits growth along <001>:
Rods become platelets

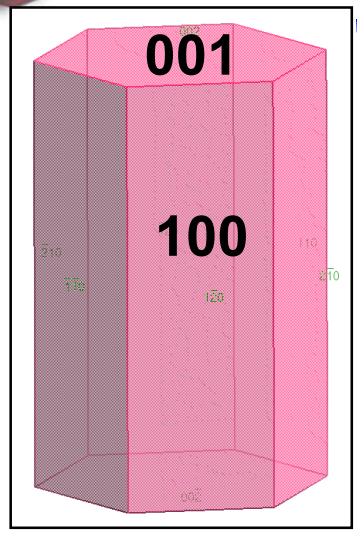


No citrate:
46 ± 6 ZnO nanorods per nucleation sites



High citrate concentration:
1-2 ZnO platelets per nucleation sites

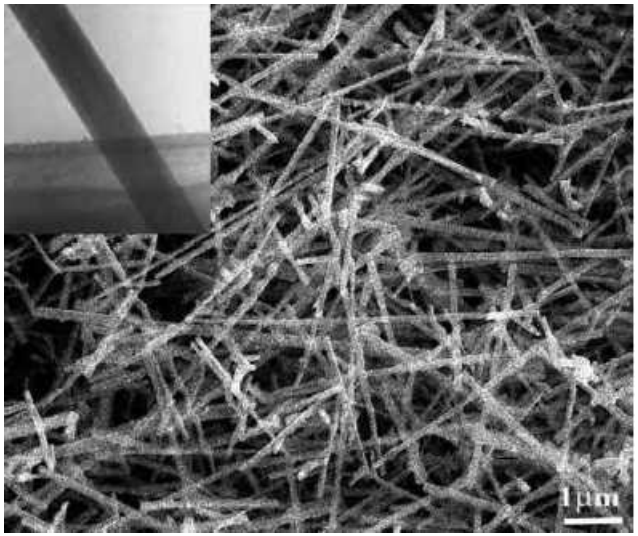
X-ray of Zincite

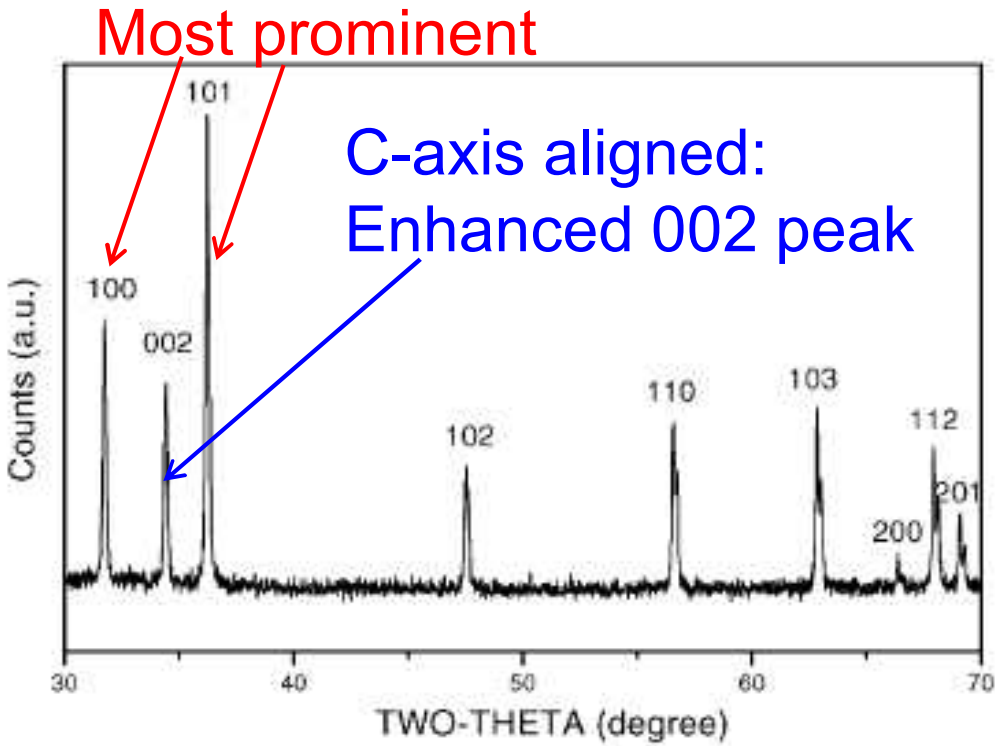


Wurtzite (hexagonal) structure:

a (in plane) = 3.250 Å

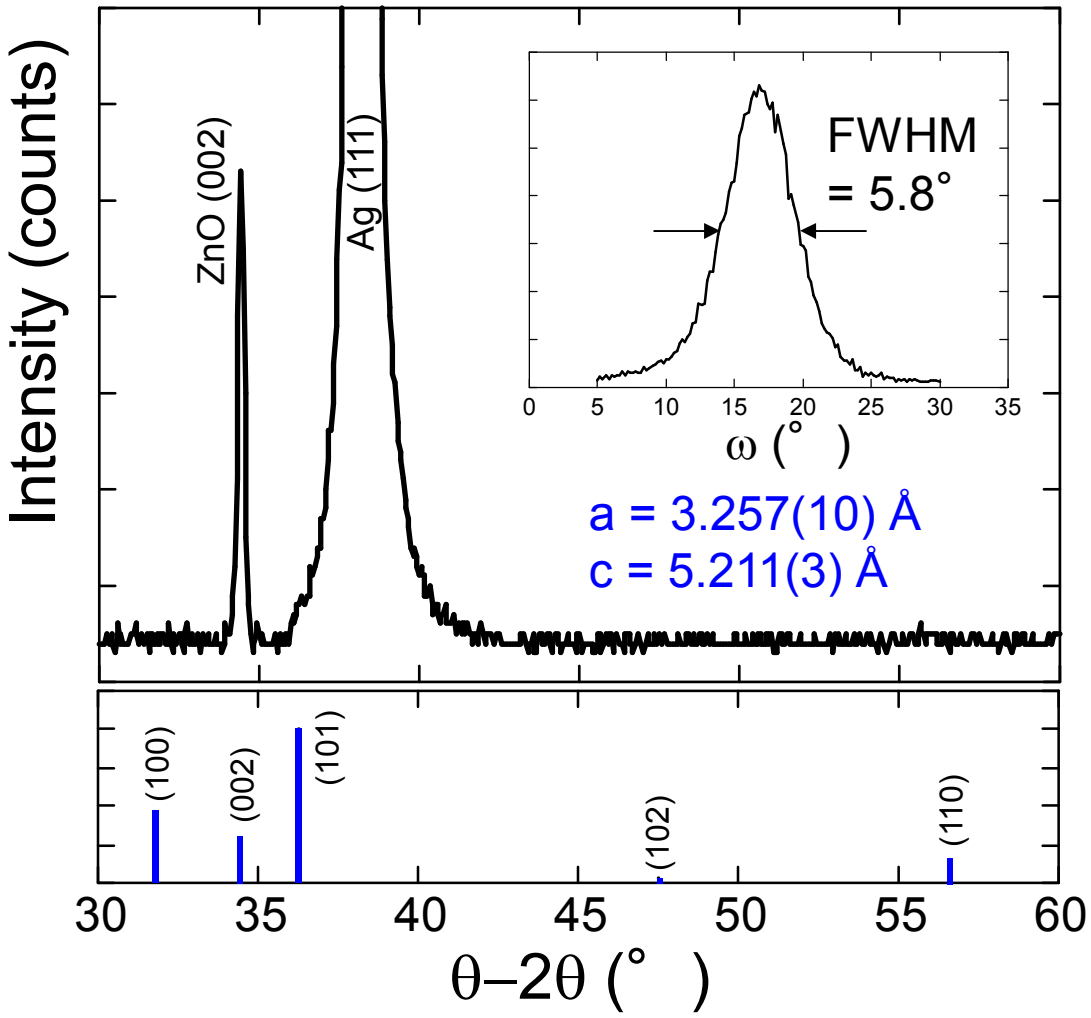
c (<001>) = 5.207 Å

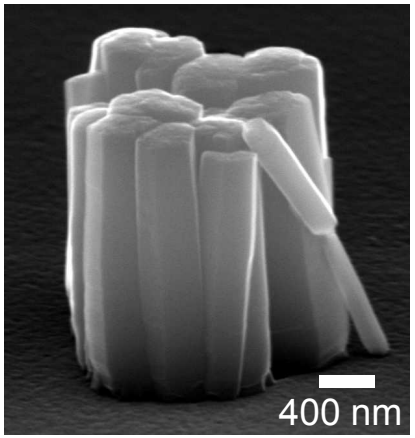


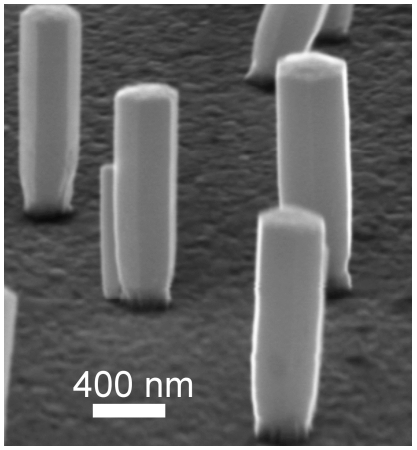


J.Y. Lee, et. al., J. Cryst. Growth 233, 5, 2001

Highly Oriented ZnO Growth





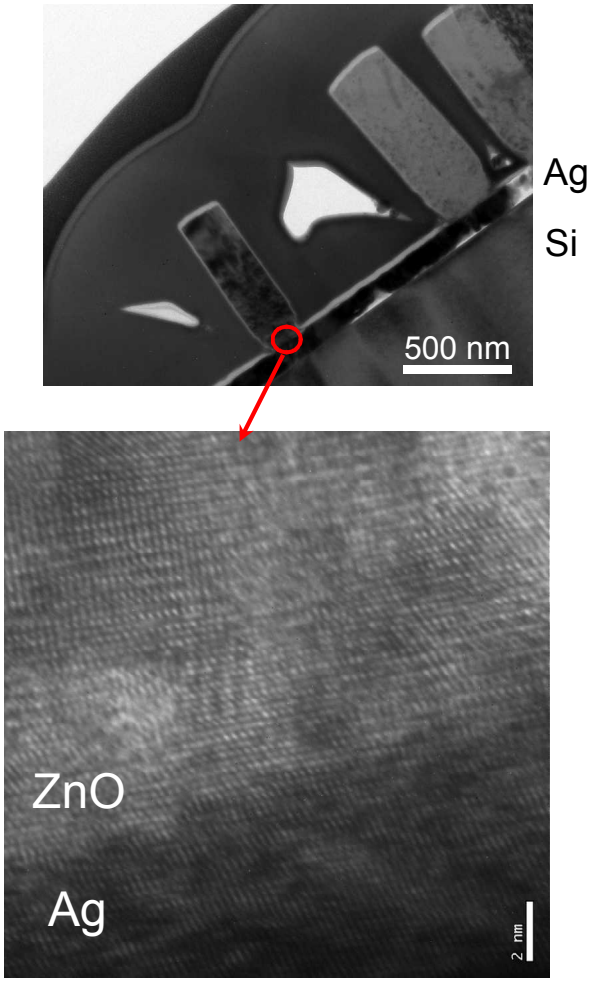


Single X'tal

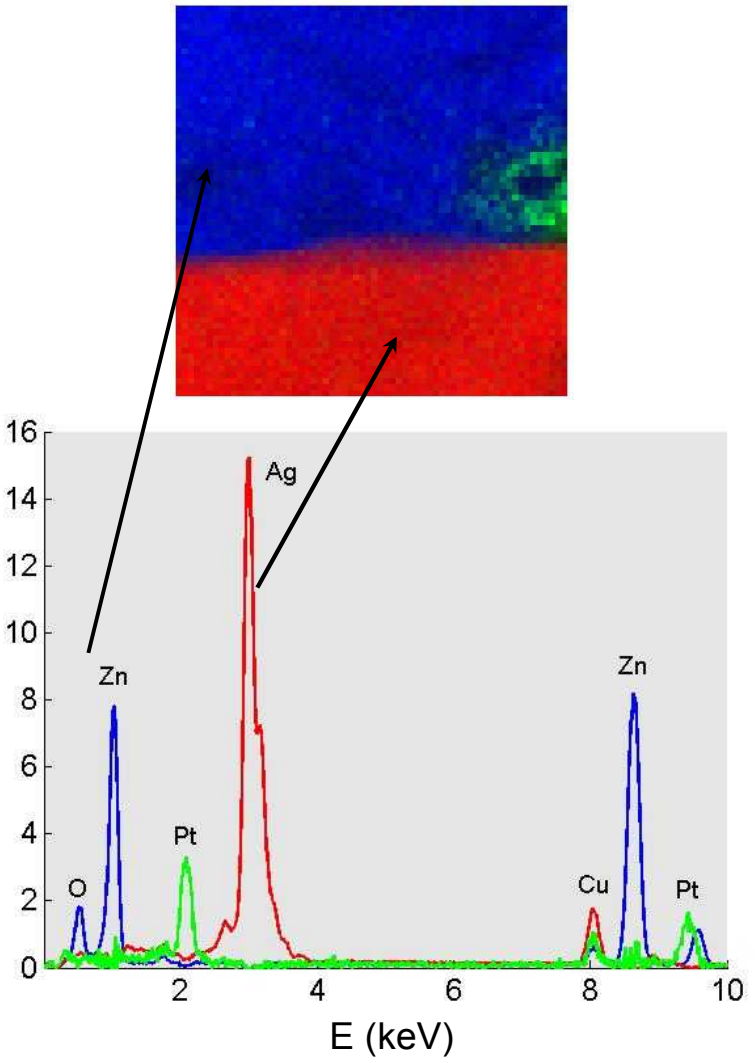
Thanks to R. G. Tissot, M. A. Rodriguez, D. L. Overmeyer

TEM Study of ZnO-Ag Interface

High resolution

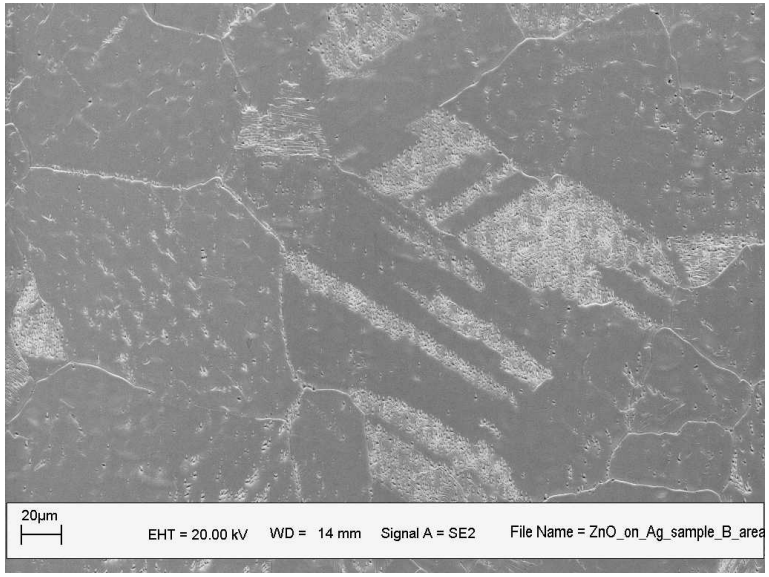


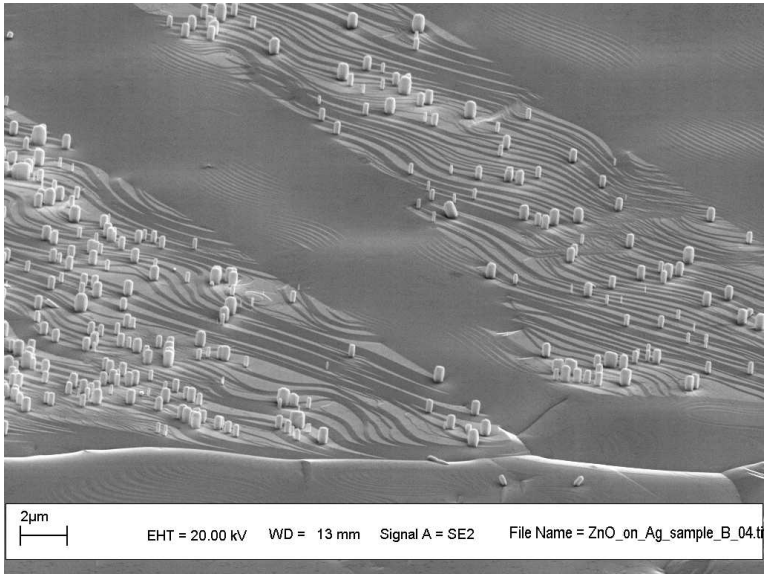
Chemical

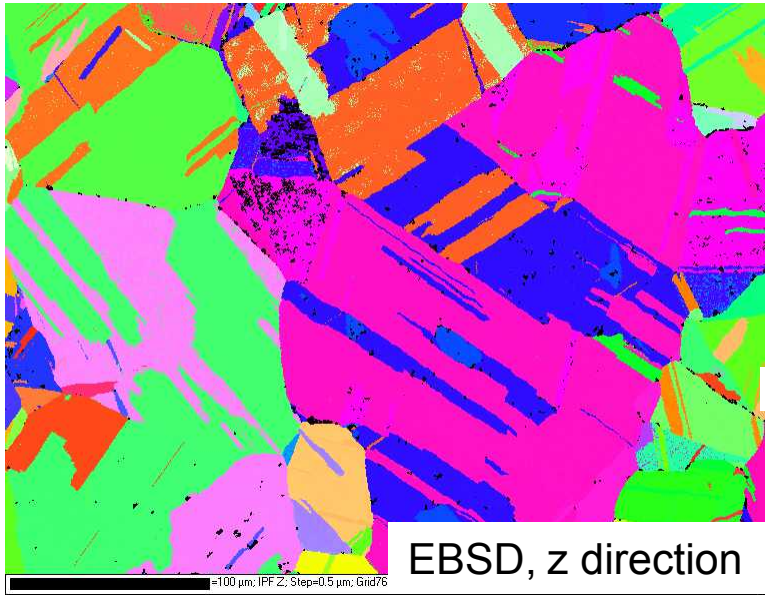


No "foreign" materials between ZnO & Ag; facetted interface. ZnO defected.

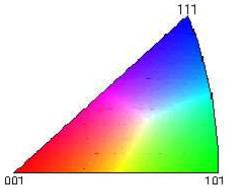
Selective Growth on Multigrain Ag







EBSD, z direction



ZnO nanorods selectively grow on <111> oriented grains, with <0001> axis perpendicular to substrate

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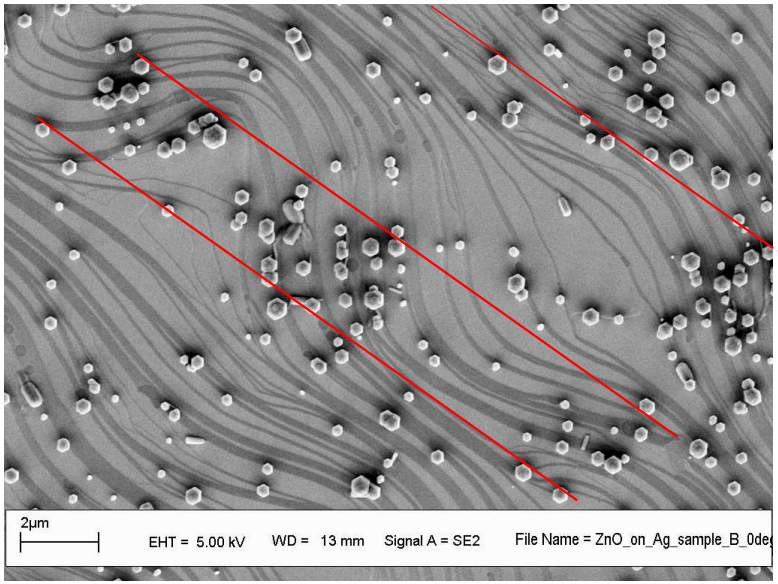
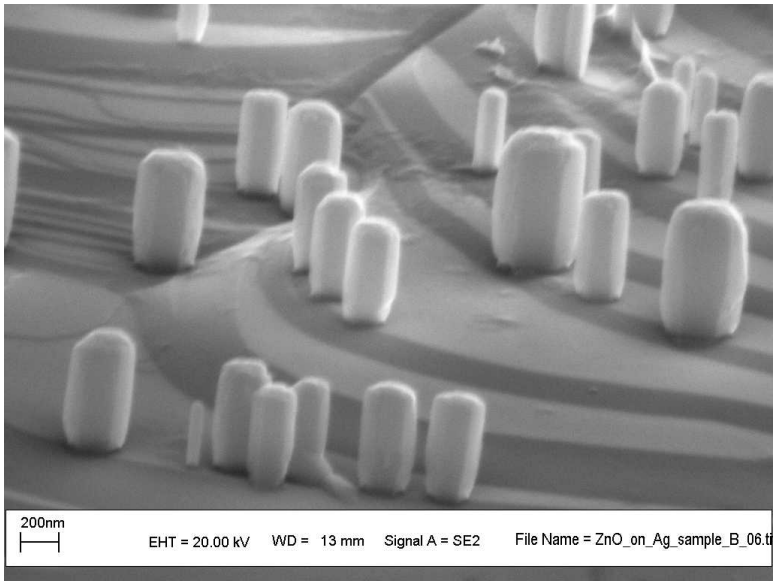
Crystallographic Alignment

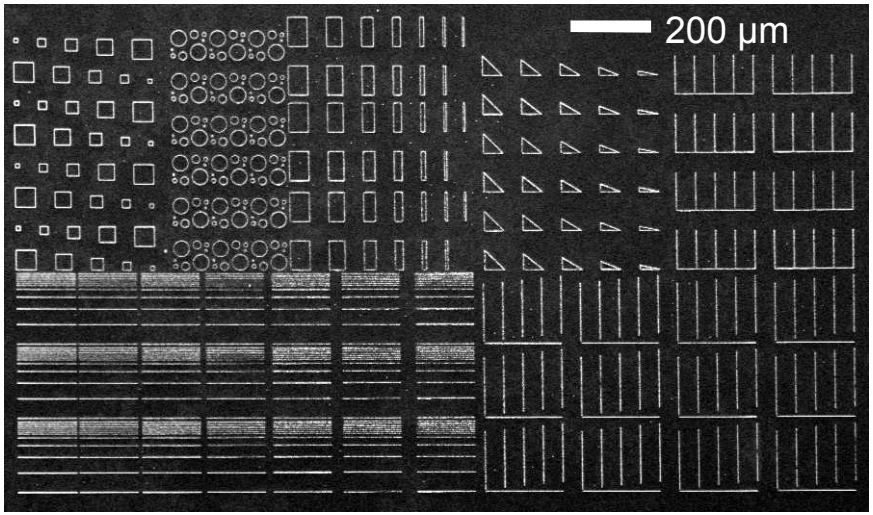


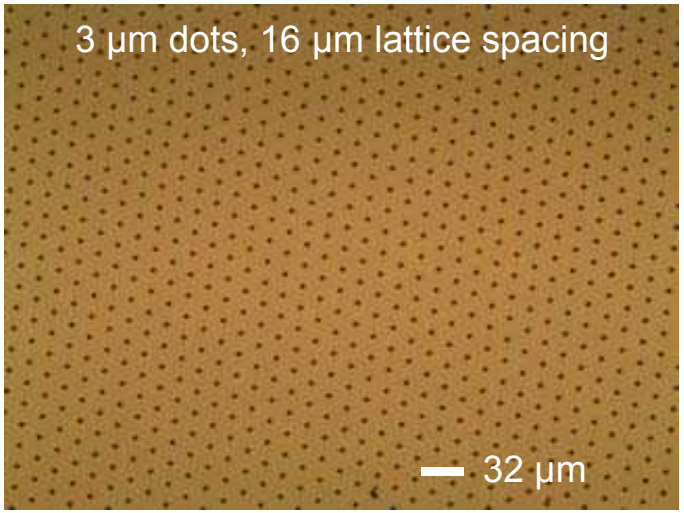


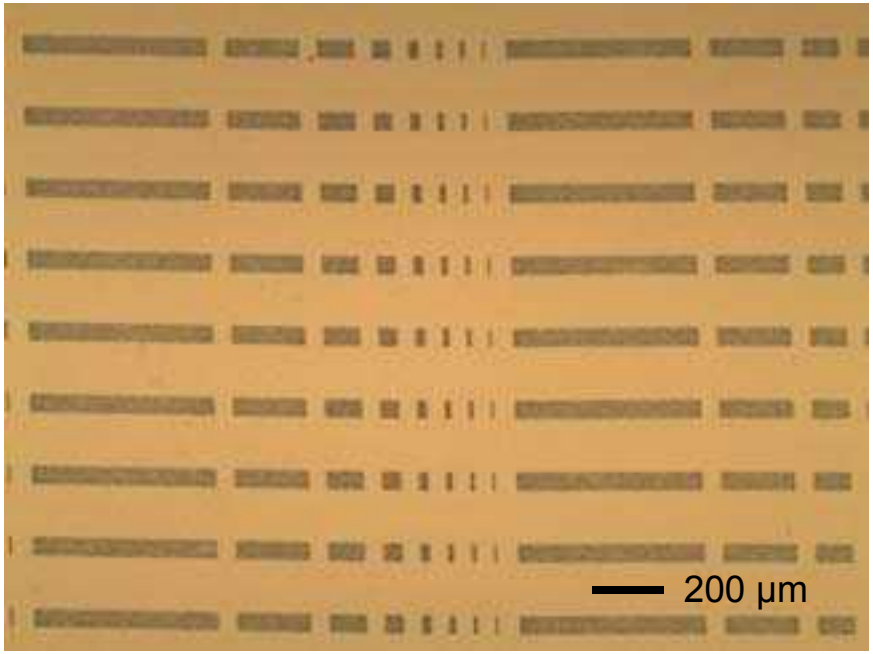
- All nanorods have the same in-plane orientation (6-fold degenerate).
- Thus, there is definite alignment between ZnO and Ag lattices.
- However, lattice mismatch > 10%?

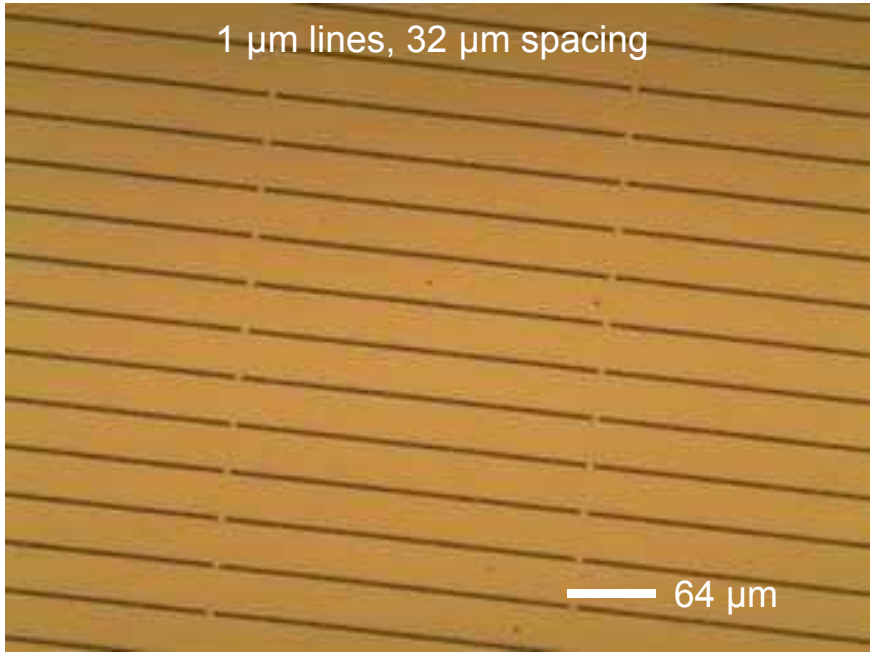
Nanorods perferentially grow at the edges of the upper terraces. Strain relief?

Large Area


200 µm

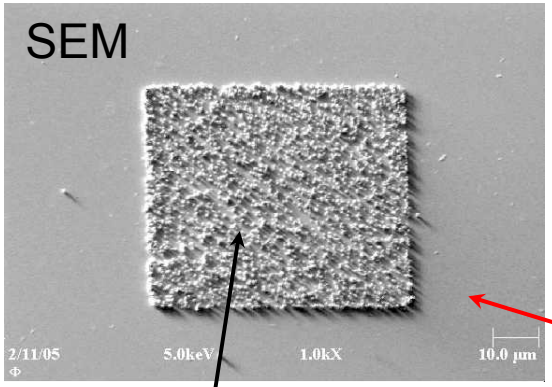

3 µm dots, 16 µm lattice spacing
32 µm

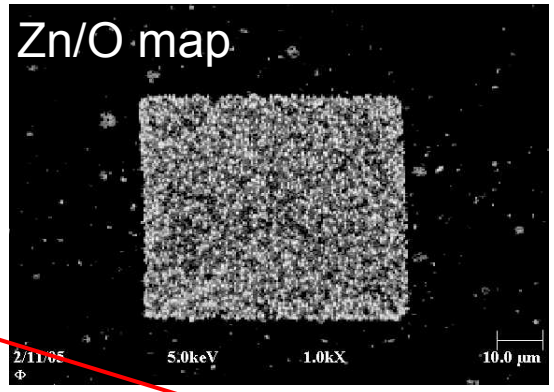

200 µm

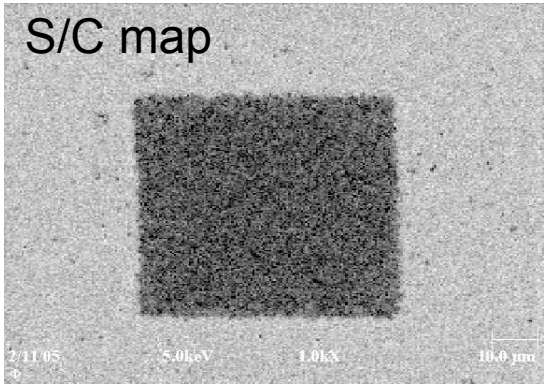

1 µm lines, 32 µm spacing
64 µm

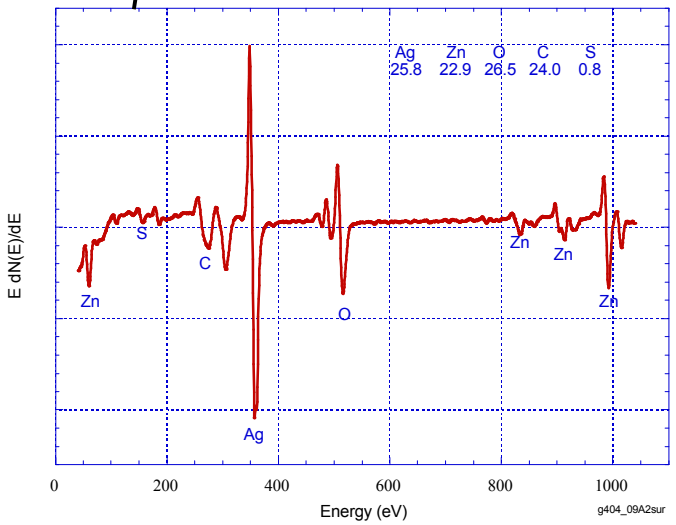
-CH_3 surface

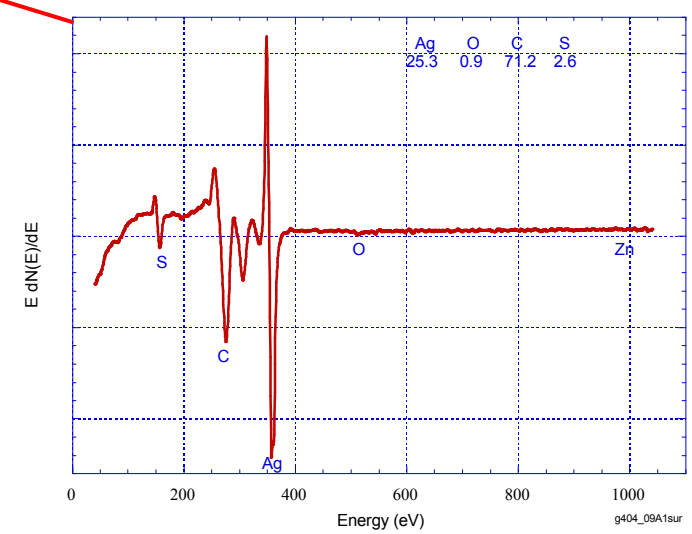
CH_3 Endgroup; after 3 hrs of growth







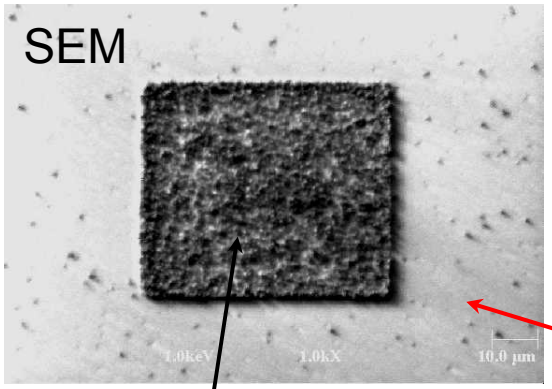


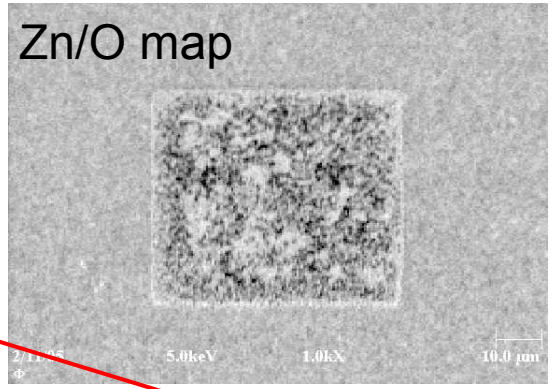


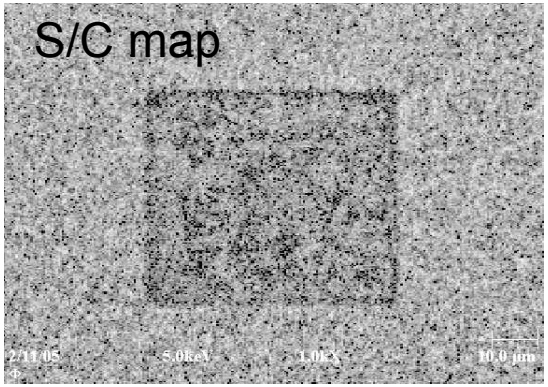
As expected: Zn & O found on no SAM regions

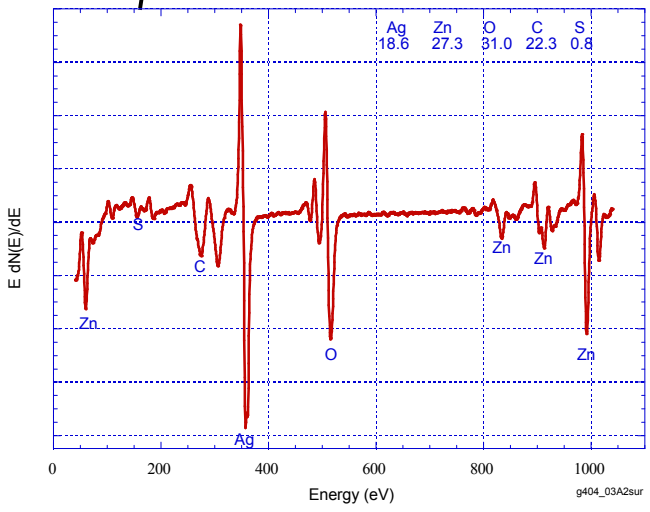
-COOH Surface (Long Time)

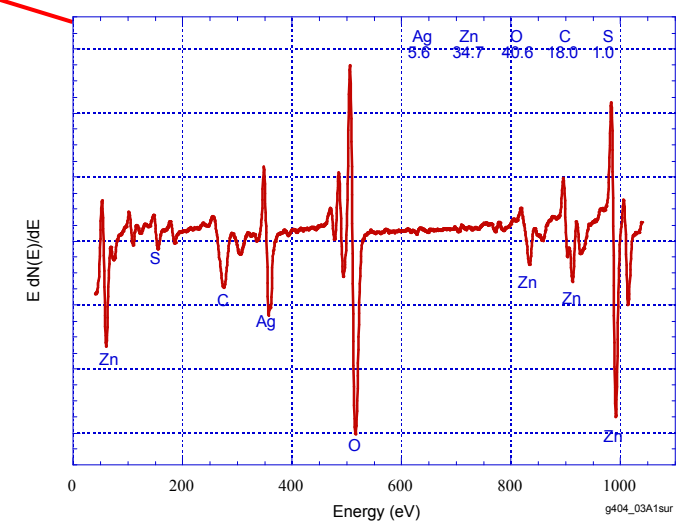
COOH Endgroup; after 3 hrs of growth







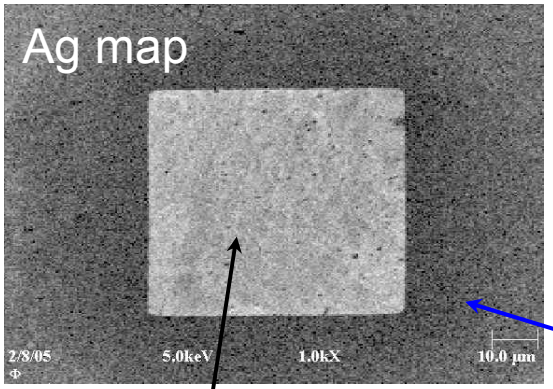


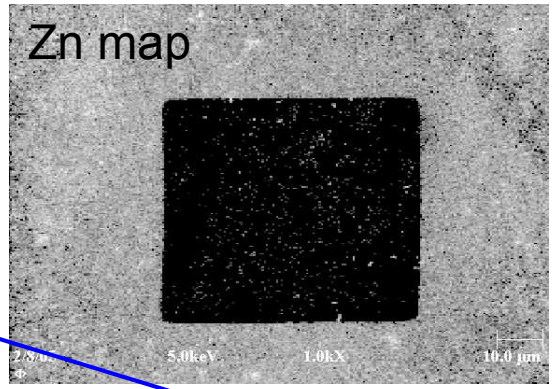


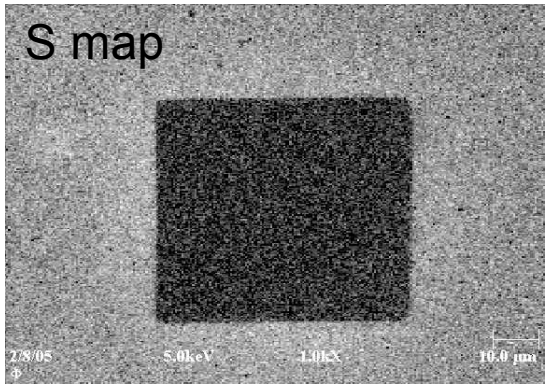
Zn & O on SAM regions, but no crystals!

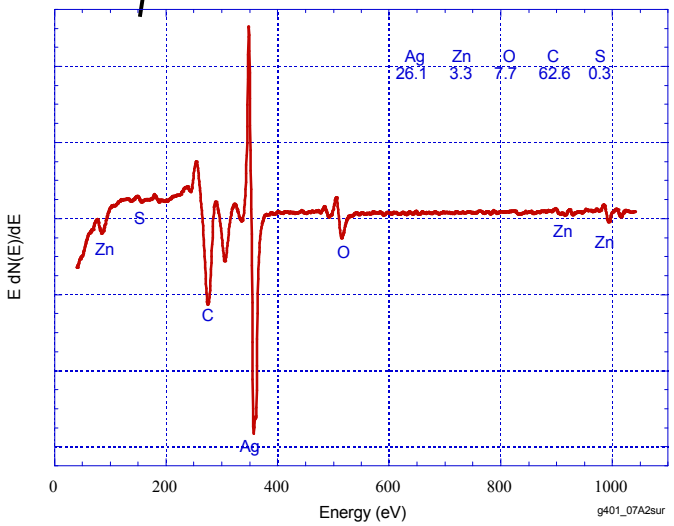
-COOH Surface (Short Time)

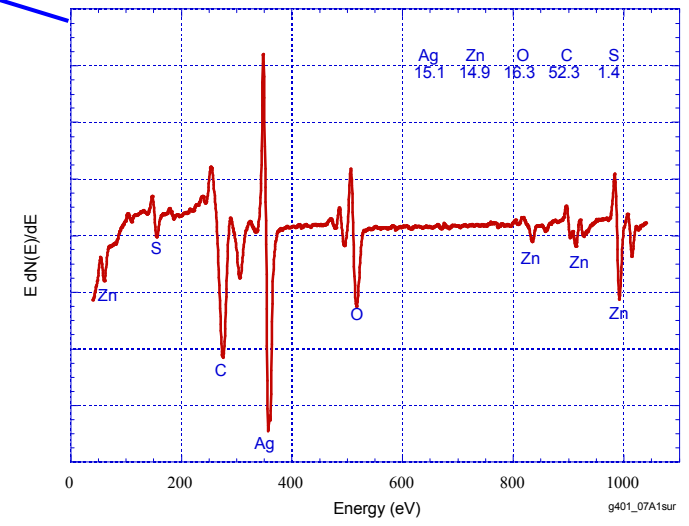
COOH Endgroup; 5 min incubation at RT











Zn has strong affinity to COO^-, as expected.
However, this is not sufficient for rod growth.

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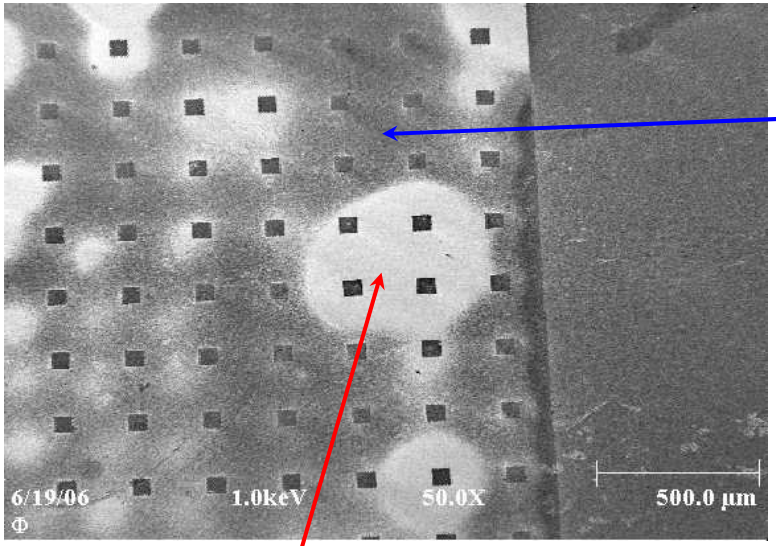
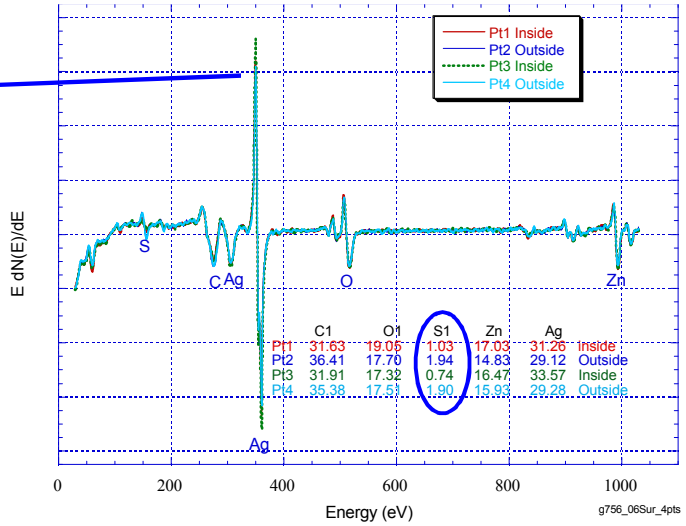
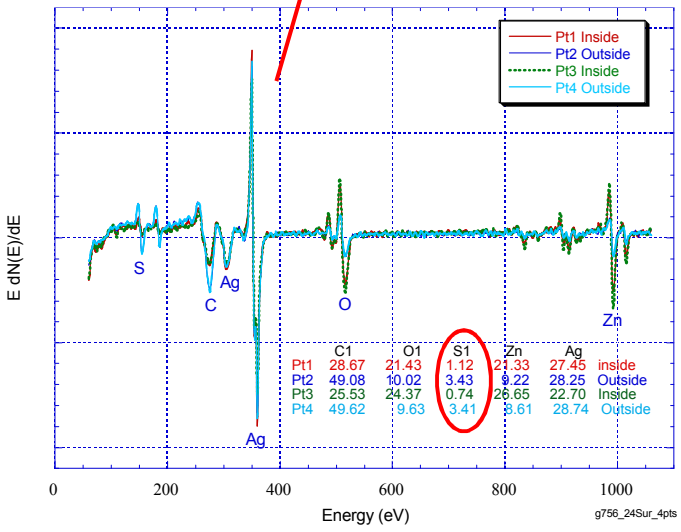
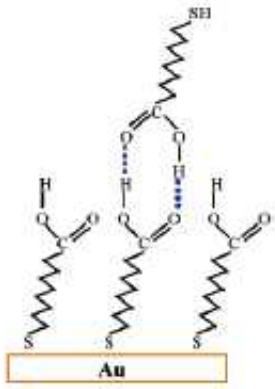
Large Scale Non-uniformity on COOH Surface



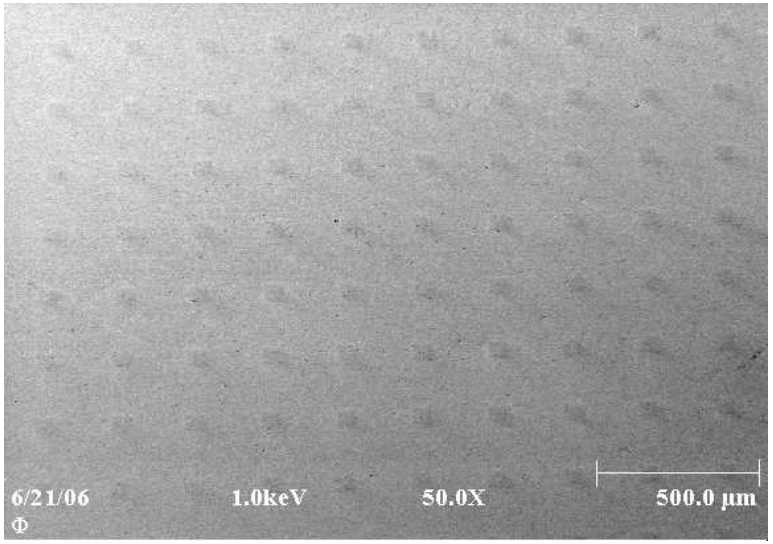


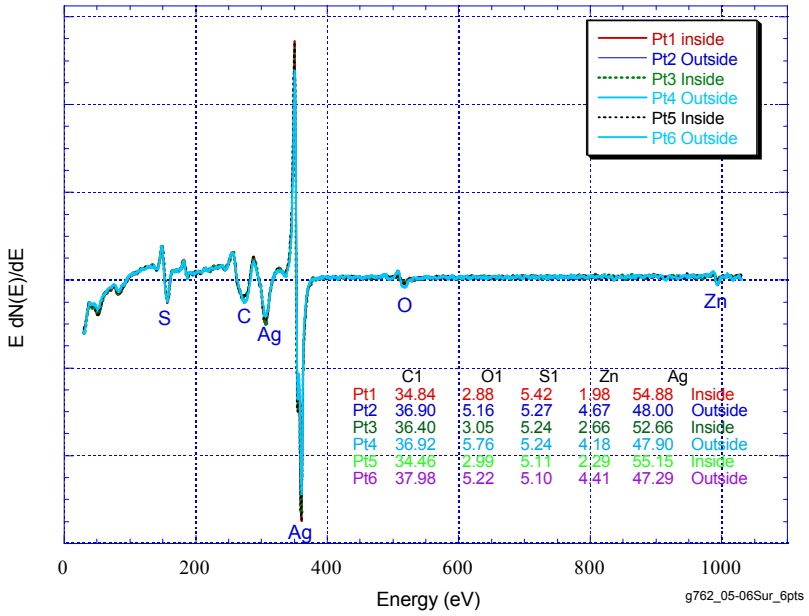


- Enhanced S signal in the SAM regions with no rods.
- Bilayers with -SH?



-SH Surface





- No optical contrast
- No ZnO nanorods anywhere
- Faint SEM contrast. S % similar between C8DT and bare Ag regions: C8DT diffusion?
- Auger detects slight enhancement of Zn & O on SAM regions
- ZnO film?
  - Zn-S: 205 kJ/mol
  - Zn-O: 159 kJ/mol

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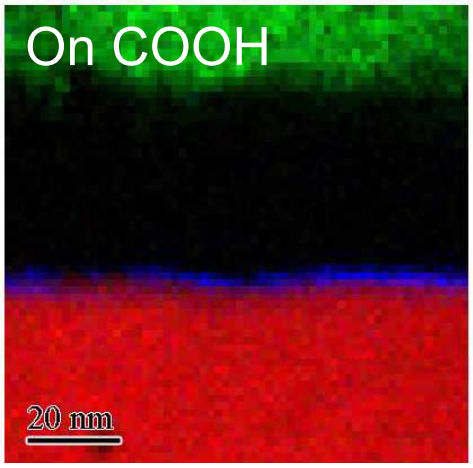
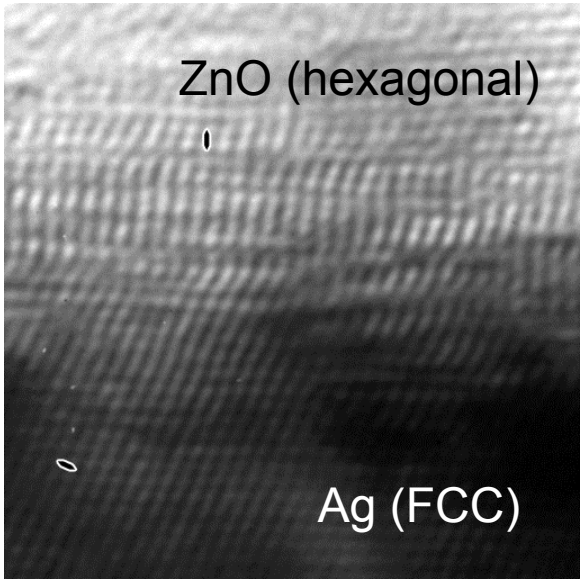
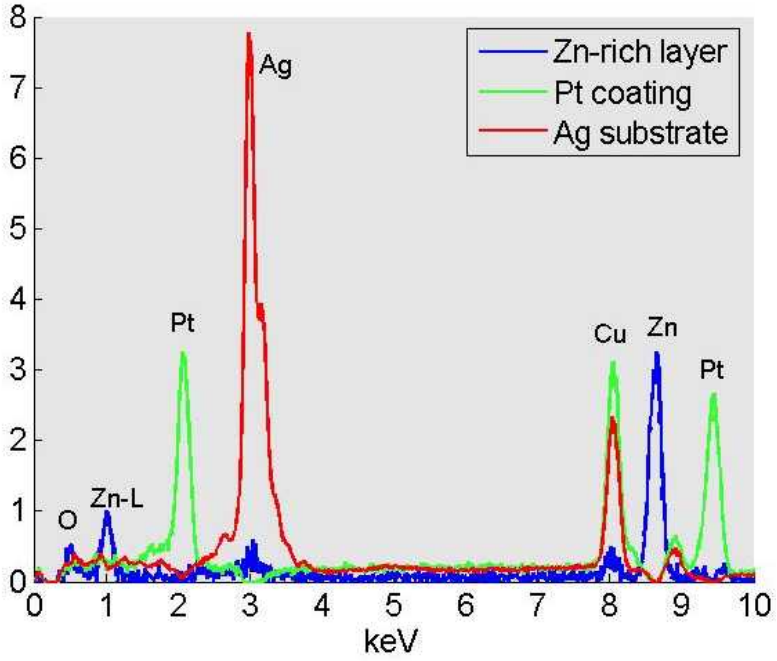
ZnO Film?







- Composite image and spectra (EDX) showing Zn-rich layer on top of Ag substrate
- HREM image showing the layer is crystalline ZnO
  - Ag d{111} 2.4 Å
  - ZnO d{0002} 2.6 Å

Summary & Outlook

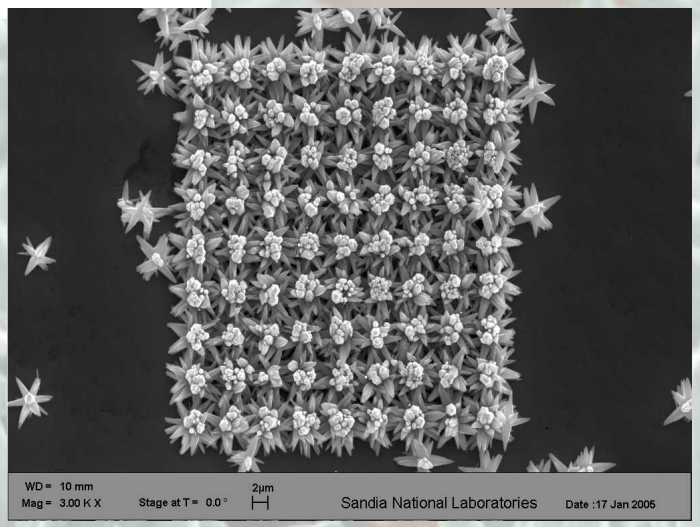
- Use organic templates to direct ZnO growth -- Demonstrate superb control in

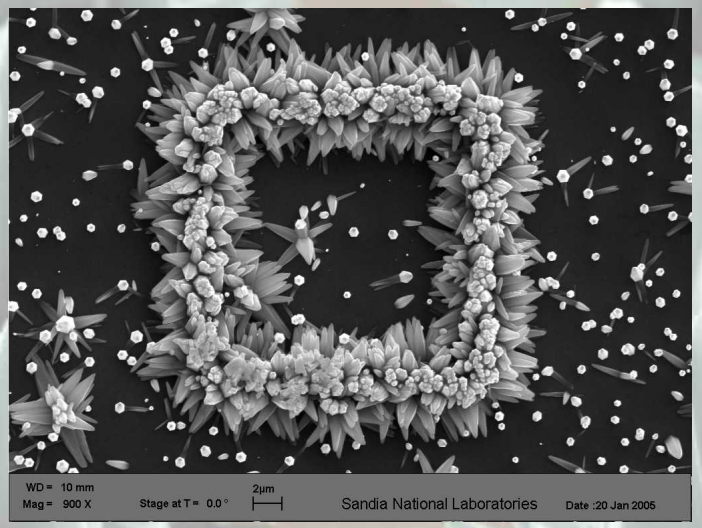
  Spatial placement, selectivity, crystal orientation, & nucleation density

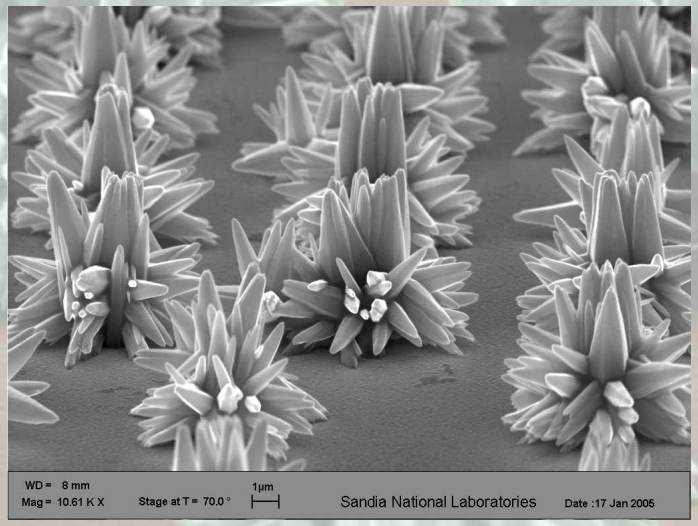
- Preferential nucleation of ZnO on Ag (111): same crystal symmetry, but no lattice match
- CH_3: no ZnO; COOH: nanorods; SH: ZnO film

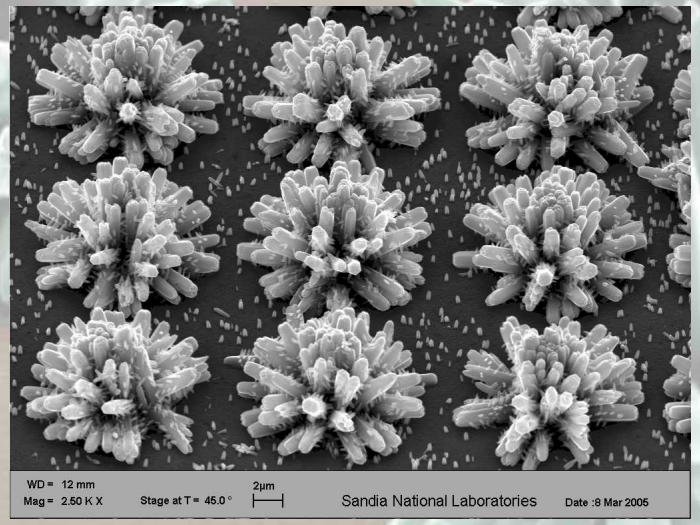
- Next
  - Understand selectivity and orientation of ZnO on (111) Ag
  - Can the SAM results be explained by interfacial energy? Is it possible to do a calculation?
  - When does ZnO grow as a film? When does it grow as rods?

Complex ZnO + Patterning









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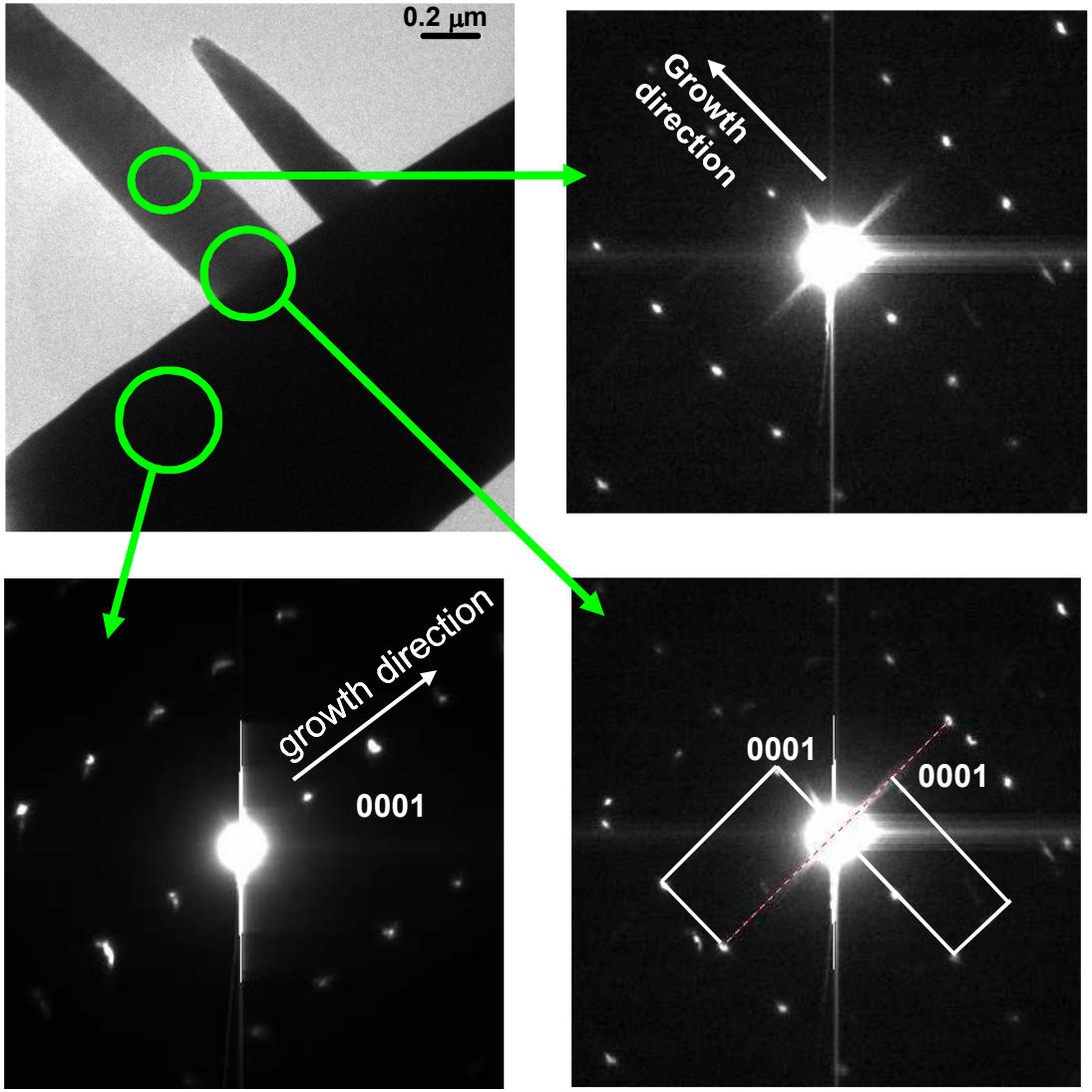
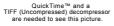
Crystal Orientation between Primary & Secondary Rods

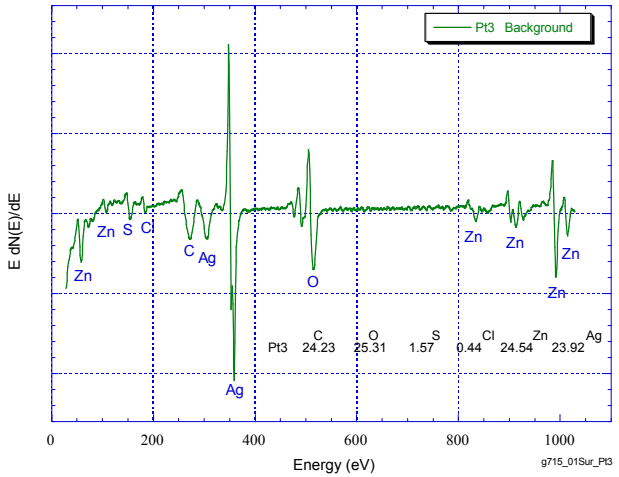


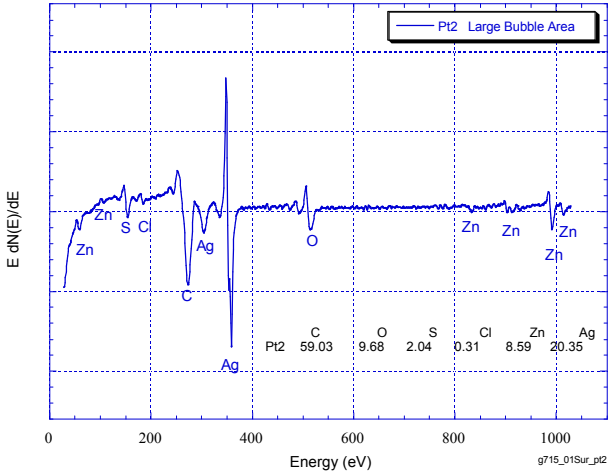
- (11-02) Twin relationship between P & S crystals
- Twin plane is not the boundary
- The boundary is the {11-00} of the primary rod and {0001-} of the secondary rods
- Could be coincidence angle: 12.3° corresponds to 7 c and $6\sqrt{3}a$
- Single direction probably due to broken inversion symmetry (in progress)

Thx to Jerry Floro

Large Scale Non-uniformity on COOH Surface







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