SAND2008-2558C

Heteroepitaxial Growth of ZnO Nanorods on Ag:

Patterned Growth, Heteroepitaxy, Nanoscale Piezoelectric and Electrical Properties

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Sandia National Laboratories

DOE BES Core Program, Sandia LDRD program,

& Truman Fellowship

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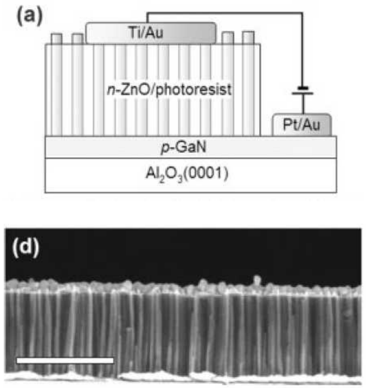
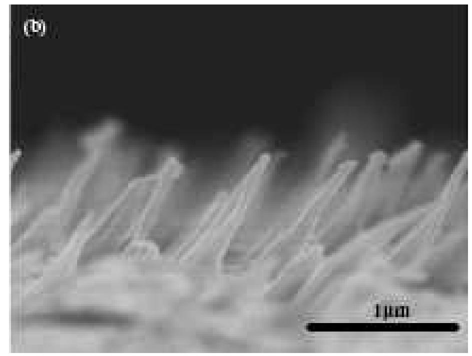
Why ZnO Nanostructures?

LEDs & lasers



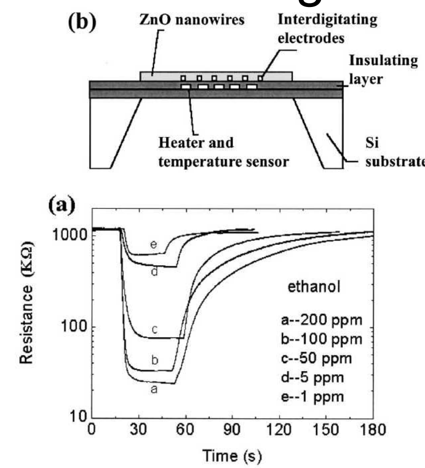
Park & Yi, AM 16, 87 (04)

Field Emission



Yang, Nanotech 16, 1300 (05)

Sensing



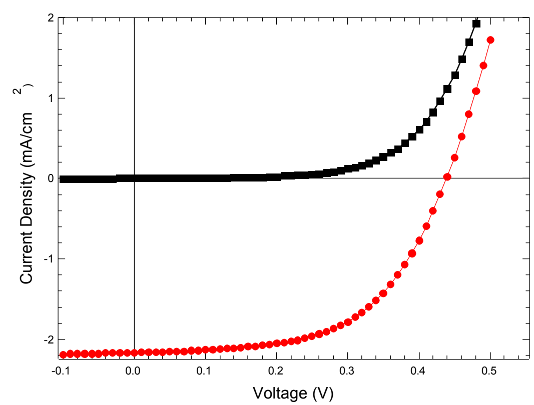
Wan, APL 84, 3654 (04)

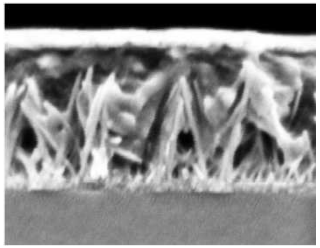
Piezoelectric Effect

QuickTime™ and a
TIFF (LZW) decompressor
are needed to see this picture.

Wang & Song, Science 312, 242 (06)

Photovoltaics





Olson, *Thin Solid Films* **496**, 26 (2006)

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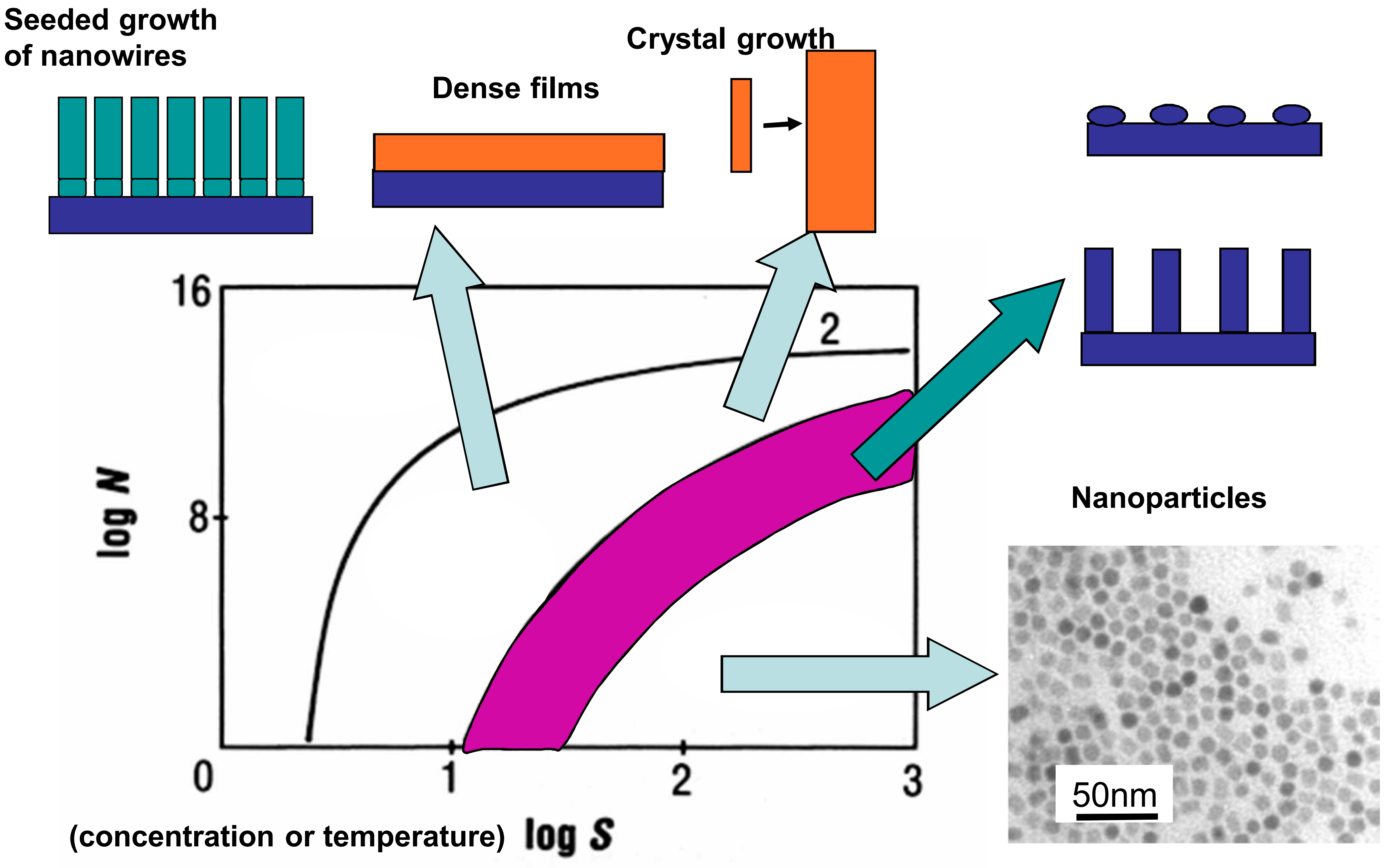
Outline

- Directed Assembly of ZnO Nanostructures
  - Direct inorganic crystal growth w/ organic templates
  - Using organic modifiers to control morphology; using multi-stage growth to create complex structures
  - Achieved control in placement, orientation, & density
- Heteroepitaxial Growth of ZnO Nanorods on Ag
  - Use EBSD to determine the relative crystal orientation of ZnO on Ag
- Piezoelectric & Electrical Properties
  - Crystal orientation
  - Piezoelectric coefficient
  - Correlation between piezoelectric coefficient and conductivity

Solution vs. Vapor Phase Growth

- Vapor
  - High temperature: > 300° C, can be as high as 1000° C
  - Most popular: VLS - Use metal catalysts
  - Great control in aspect ratio, crystal orientation, shape
  - Difficult to achieve large area uniformity
  - Costly
- Solution
  - Low temperature: < 100° C
  - No catalyst needed
  - Environmentally benign
  - Complex, wide variation of shapes
  - Large area scaling possible
  - Potential inexpensive manufacturing
  - Crystal morphology can be manipulated through solution chemistry using *organic* modifiers

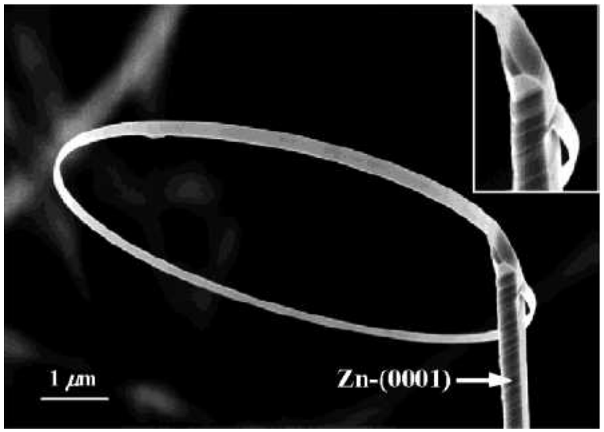
Solubility Diagram for Controlled Nucleation



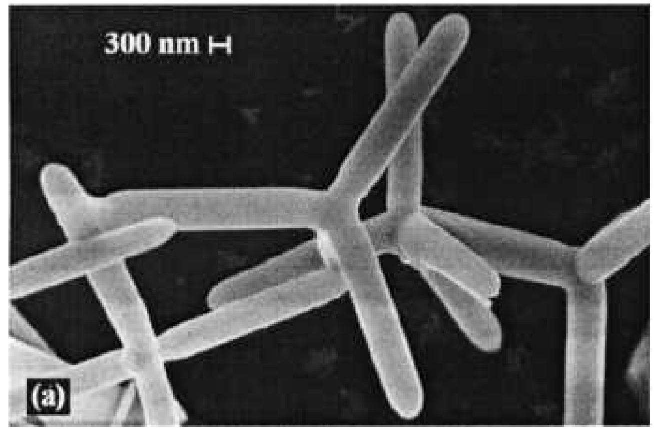
Bunker et al. Science, 264, 48, 1993

Motivation for Assembly

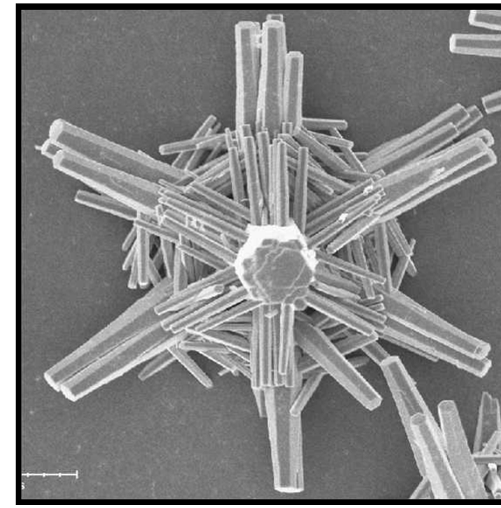
Complex ZnO Nanostructures



Nanobelt
Georgia Tech



Tetrapods
U. Hong Kong

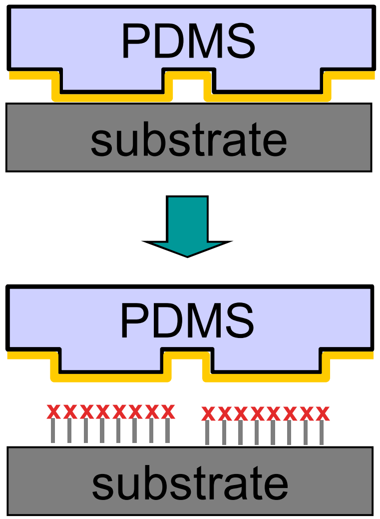


Hierarchical nanostructures, Sandia

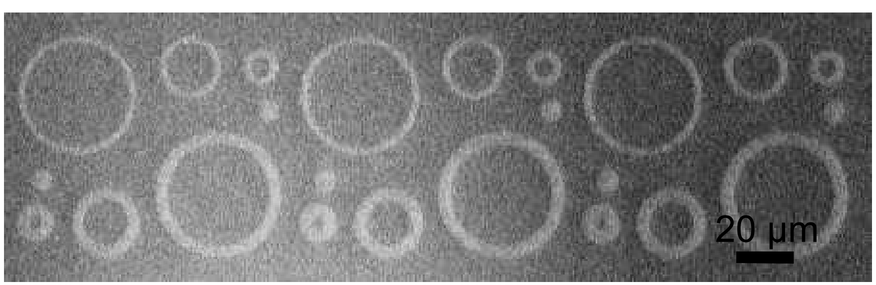
- Explosion in nanomaterials synthesis
- To make these new materials useful:

  (Directed) Assembly -- placement, density, orientation
- Conventional 2D lithography inadequate

Microcontact Printing

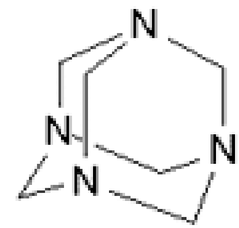


$HSC_{10}H_{20}COOH$
$HSC_{15}H_{30}CH_3$



Solution Growth

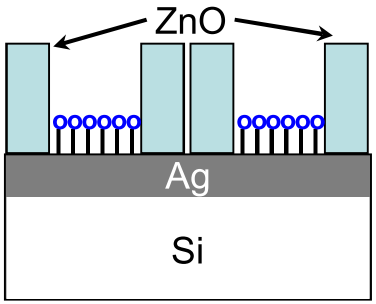
- Dilute $Zn(NO_3)_2$ + HMT

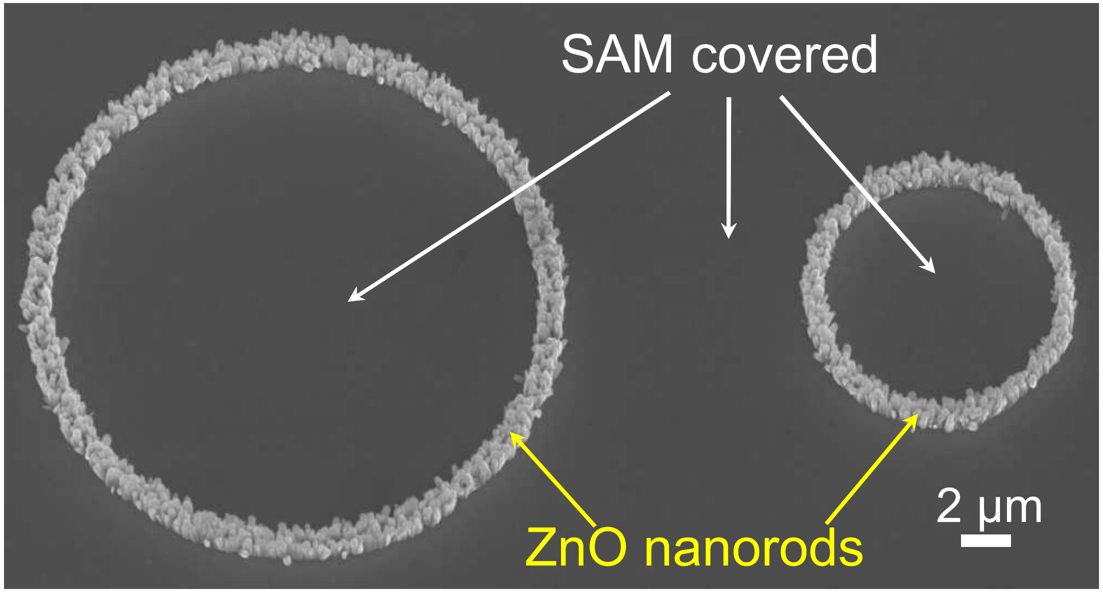


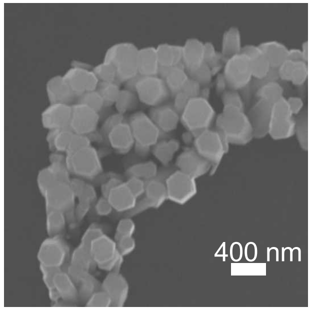
- T = 55 - 65 ° C
- Time = 2 to 6 hrs
- ZnO growth mediated by HMT degradation
- Demonstrate control in
  - spatial placement
  - crystal orientation
  - nucleation density

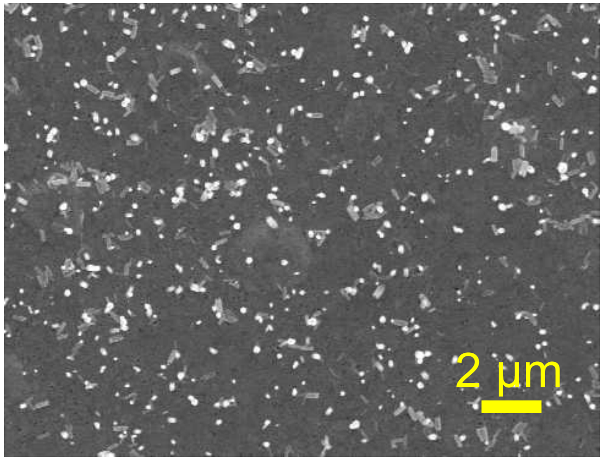
Nano Lett 5, 83 (2005)

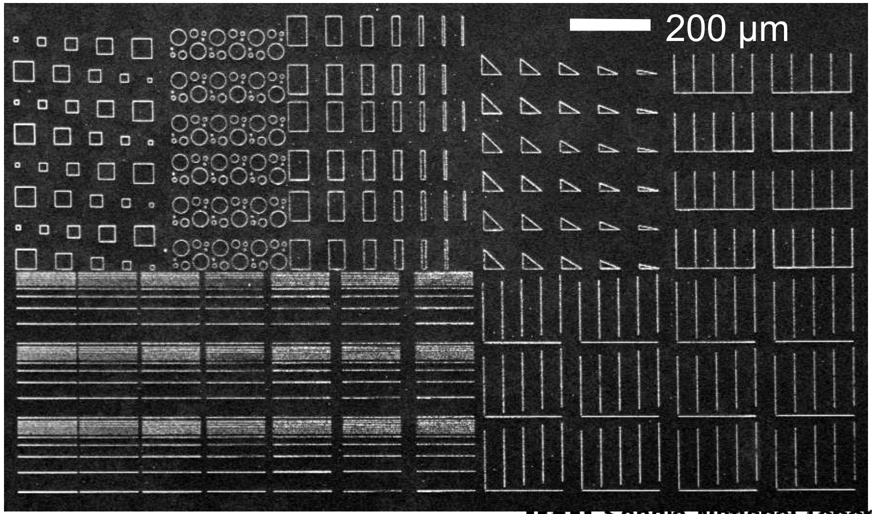
Selective ZnO Growth on Ag





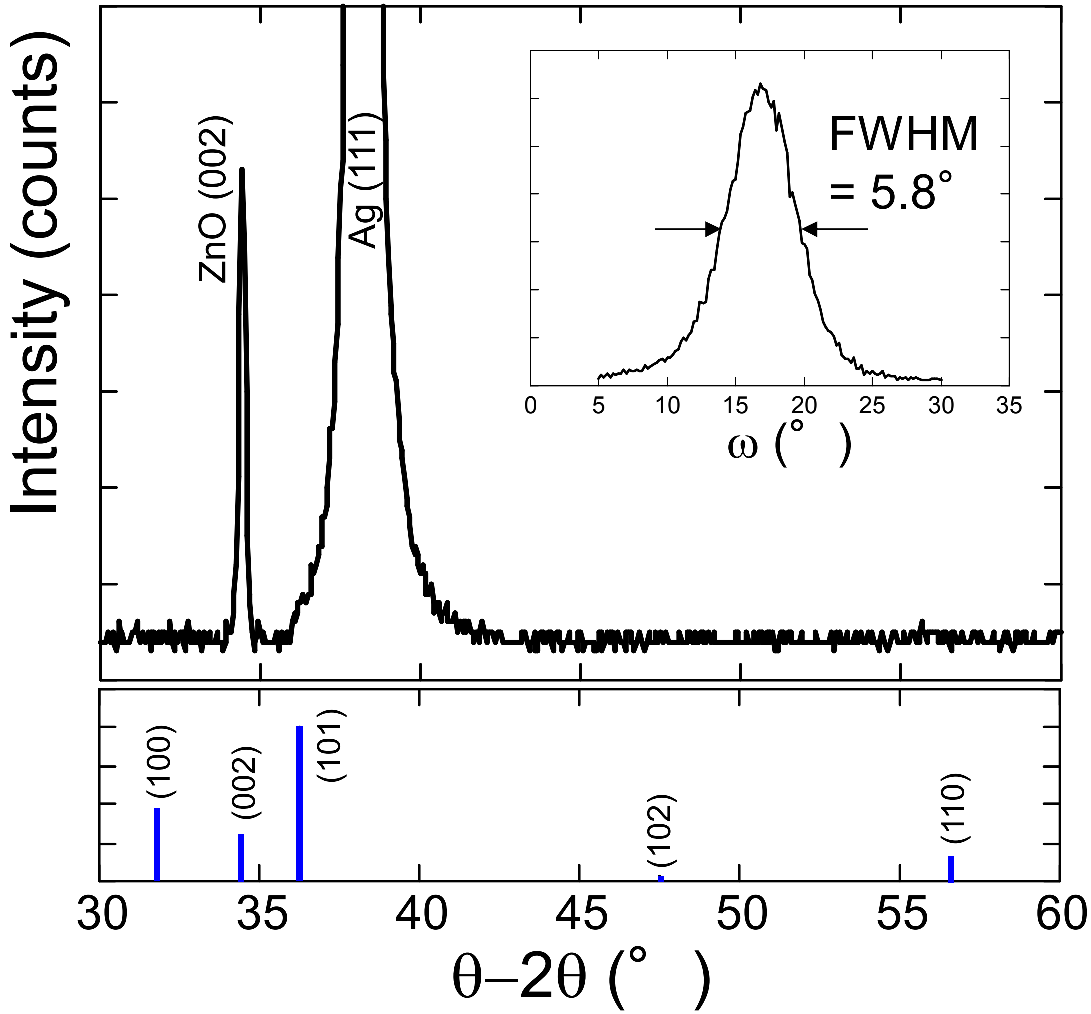


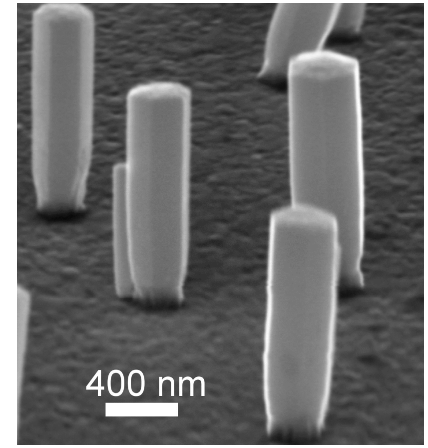




Nano Lett 5, 83 (2005)

Highly Oriented ZnO Growth

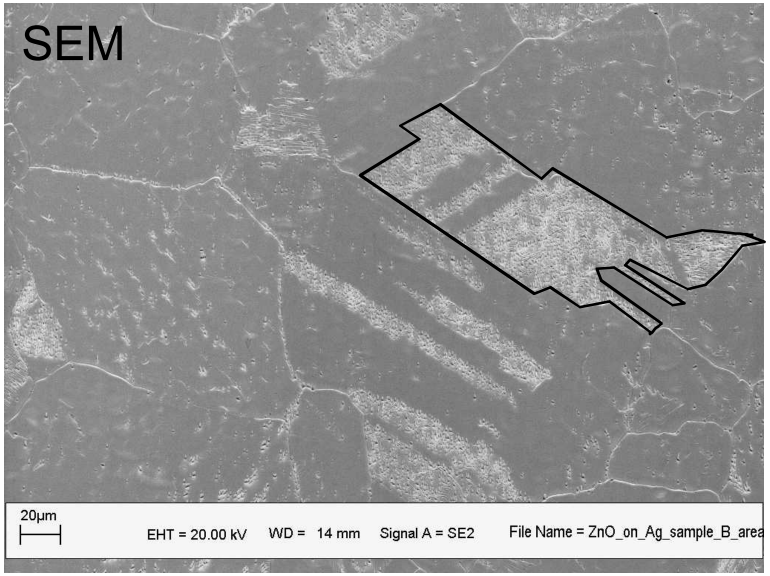


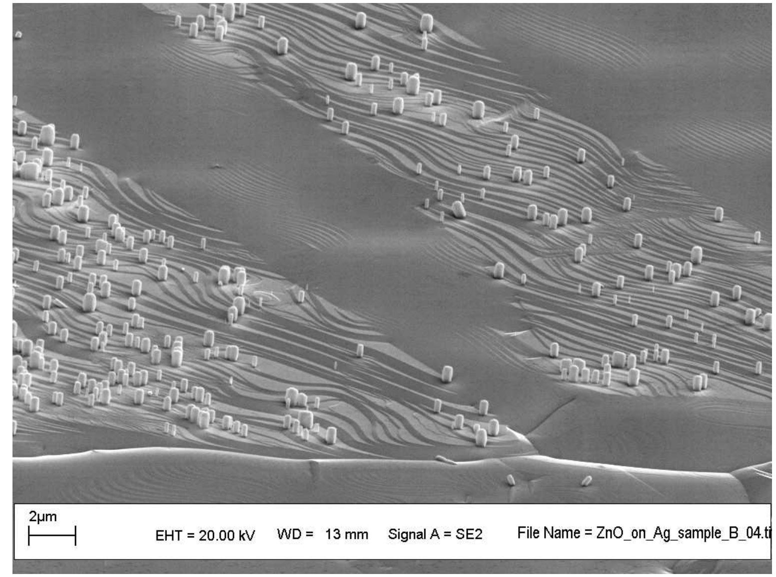


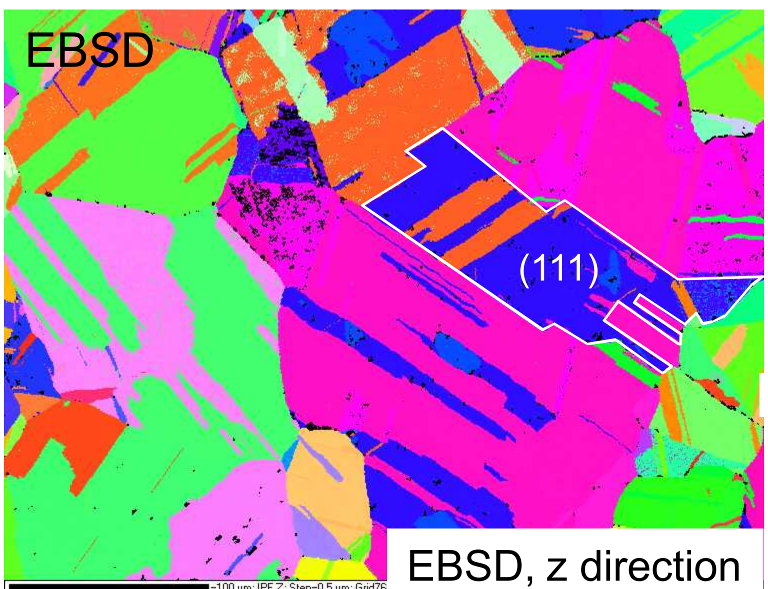
- Ag: fcc
  a = 4.08 Å
- ZnO: wurtzite
  a = 3.25 Å
  c = 5.21 Å
- 11% mismatch

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

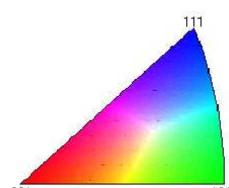
Selective Growth on Ag Polycrystals





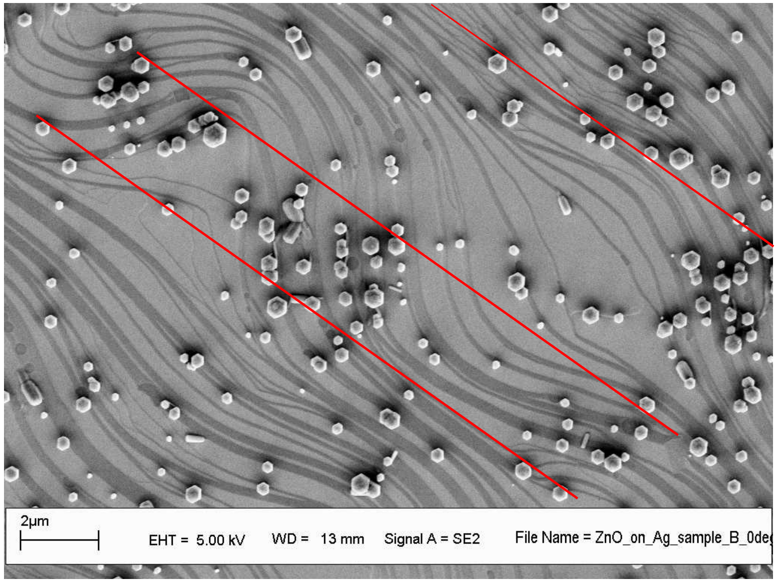


EBSD, z direction

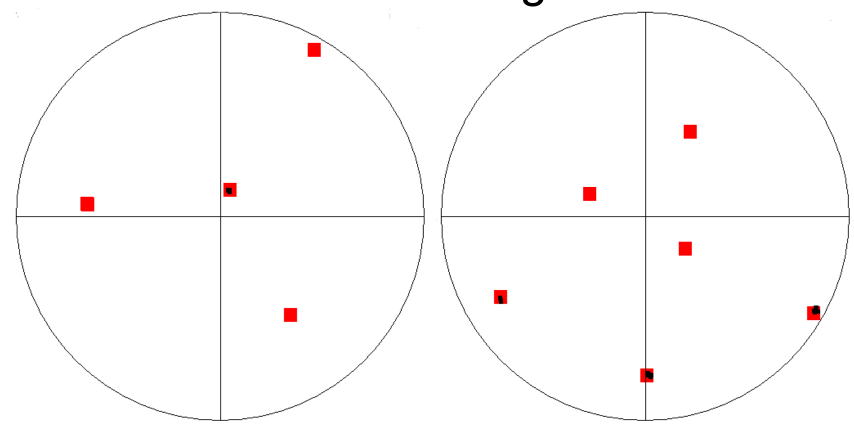


ZnO nanorods selectively grow on <111> oriented grains, with <0001> axis perpendicular to substrate

Crystallographic Alignment



EBSD Pole Figures

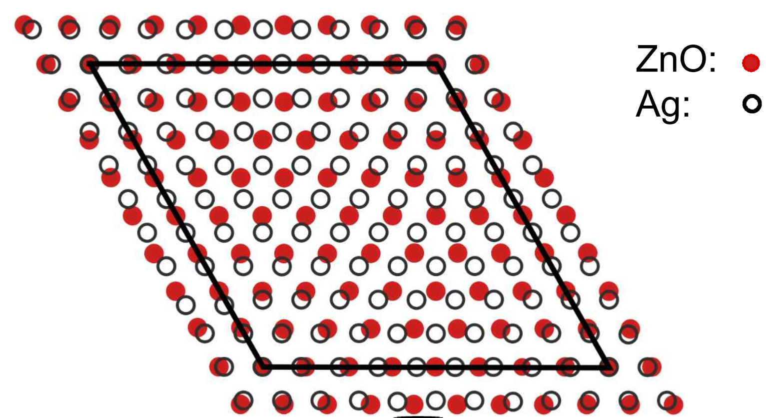


Ag <111>
ZnO <0001>

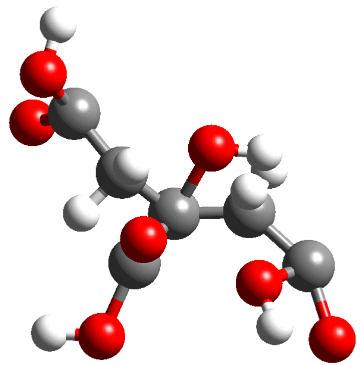
Ag [110]
ZnO $[11\bar{2}0]$

- All nanorods have the same in-plane orientation also.
- EBSD:
  - **ZnO <0001> || Ag <111>**
  - **ZnO $< 11\bar{2}0 >$ || Ag $< 1\bar{1}0 >$**
  - (within 1°)
- However, lattice mismatch > 10%.

"Hex on Hex"

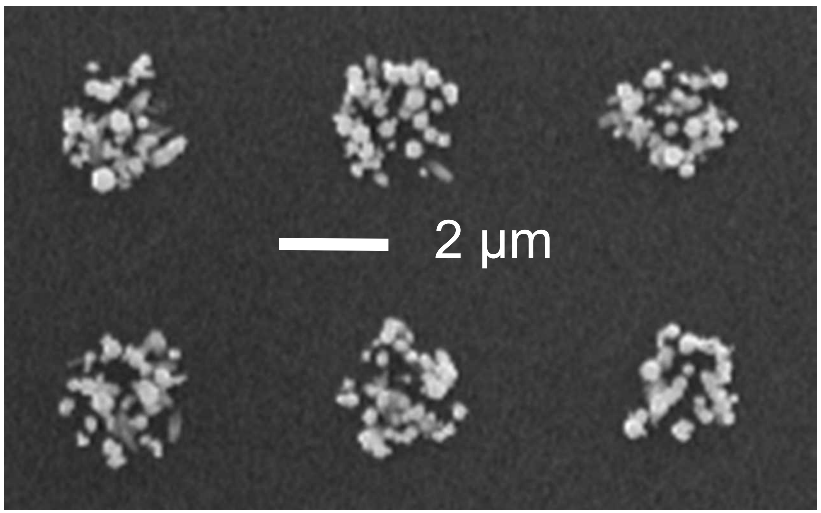


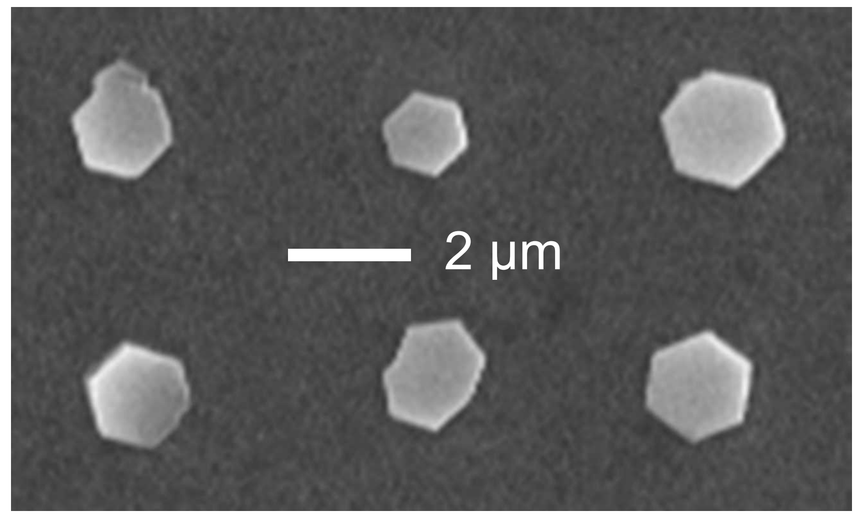
Nucleation Density Control: Growth Modifier



Citrate inhibits growth along <001>:
Rods become platelets

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



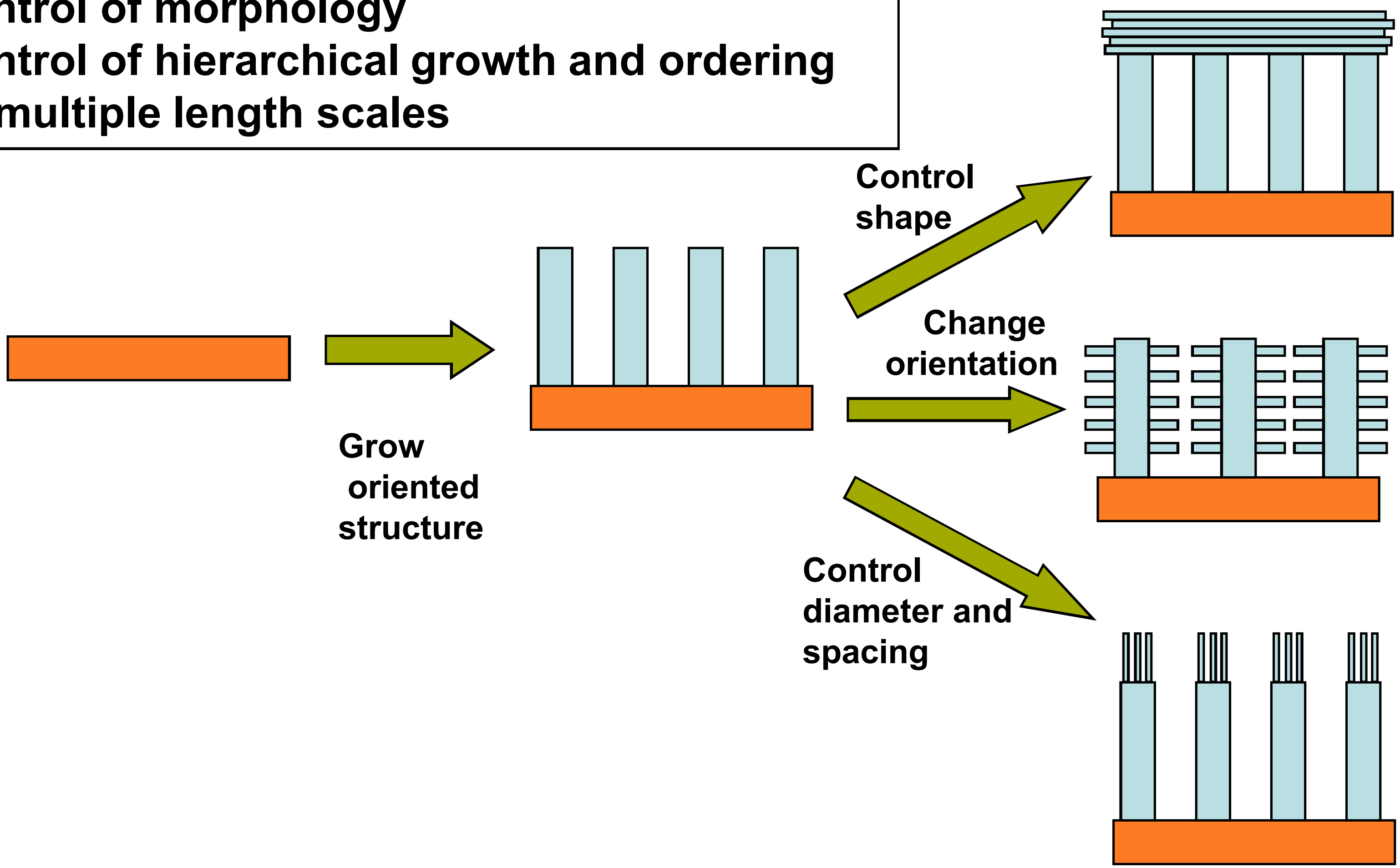


No citrate:
46 ± 6 ZnO nanorods per nucleation sites

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

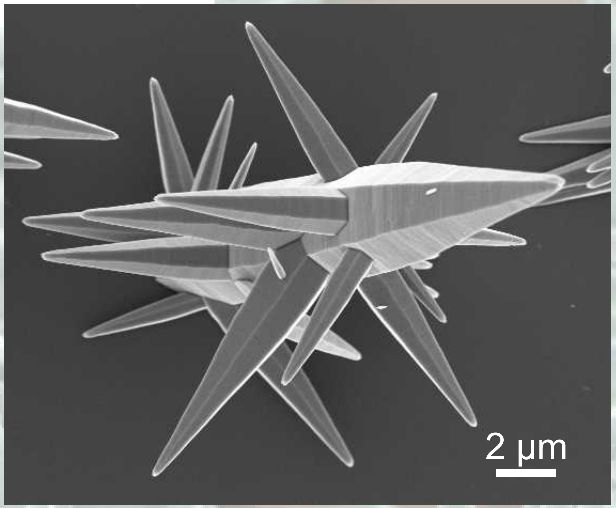
Growth of Complex Nanostructures through Controlled Chemical Synthesis

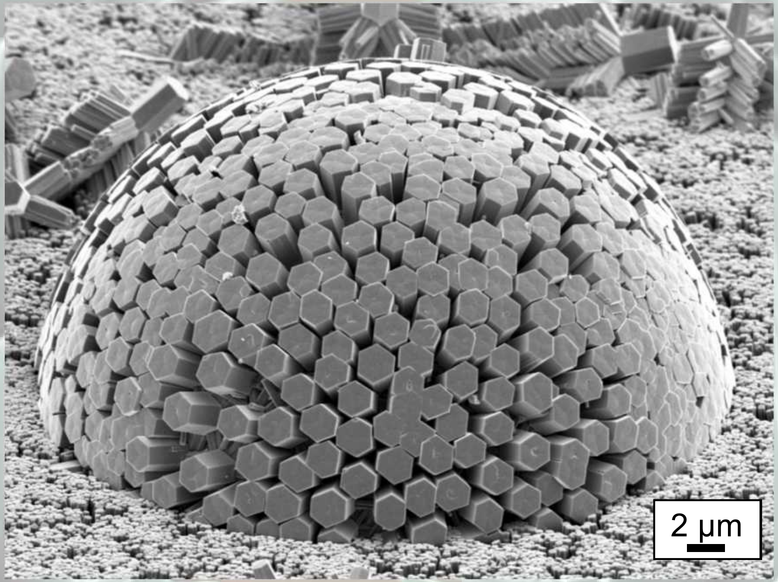
1. Control of nucleation, growth and orientation
2. Control of morphology
3. Control of hierarchical growth and ordering on multiple length scales

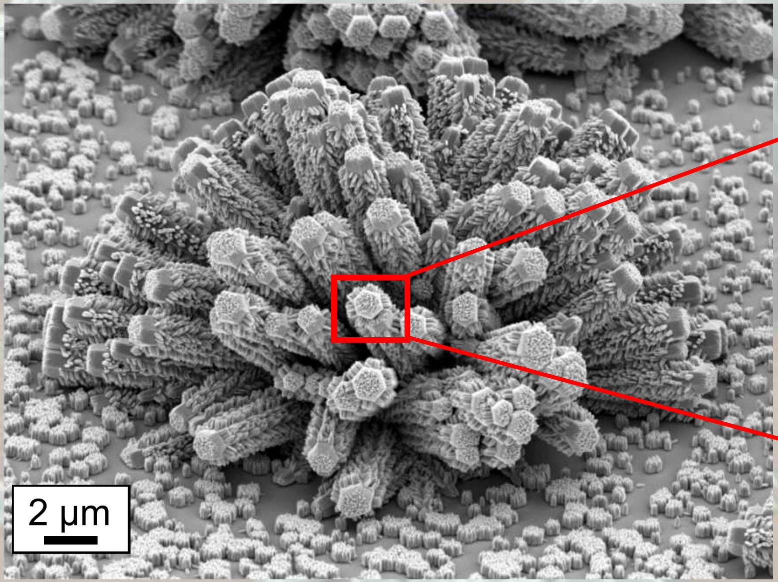


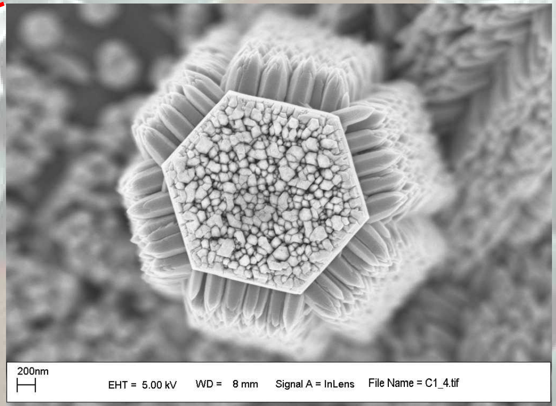
Adv Func Mater 16, 335 (2006)

Complex ZnO Nanostructures









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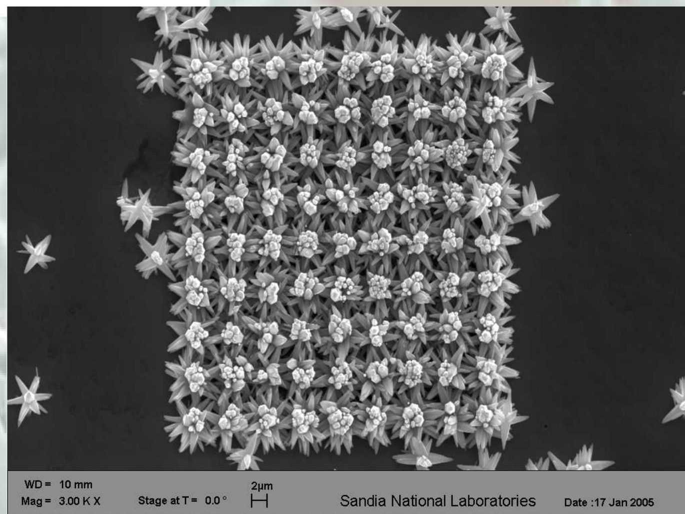
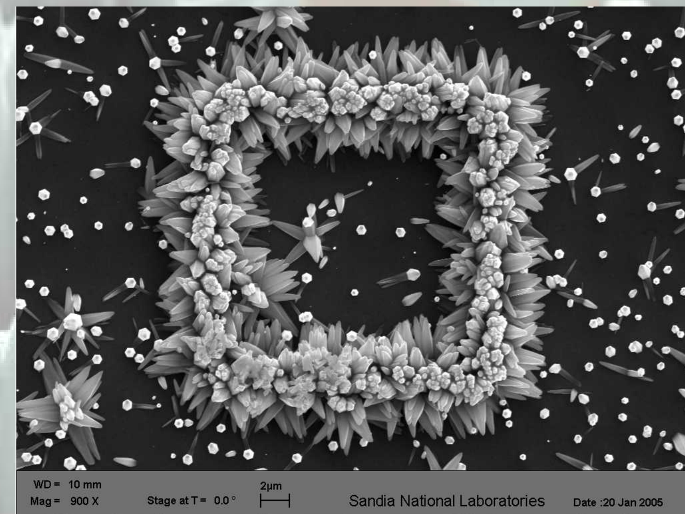
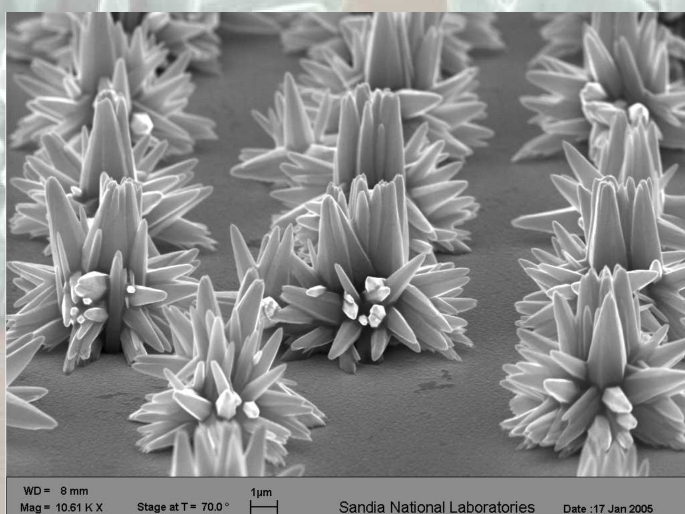
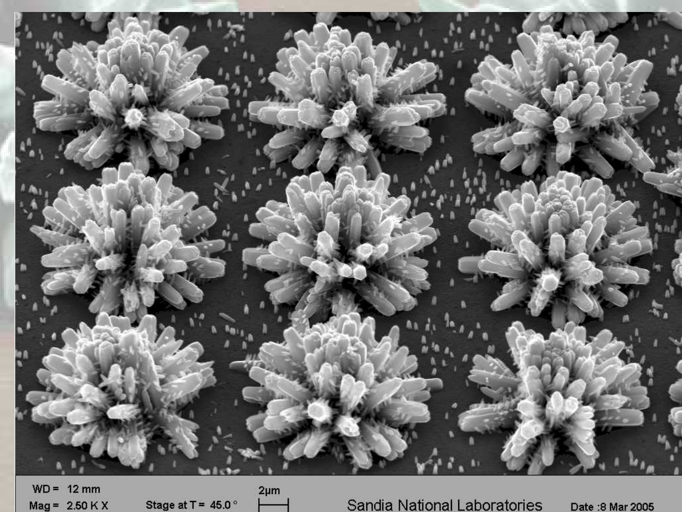
Complex ZnO + Patterning









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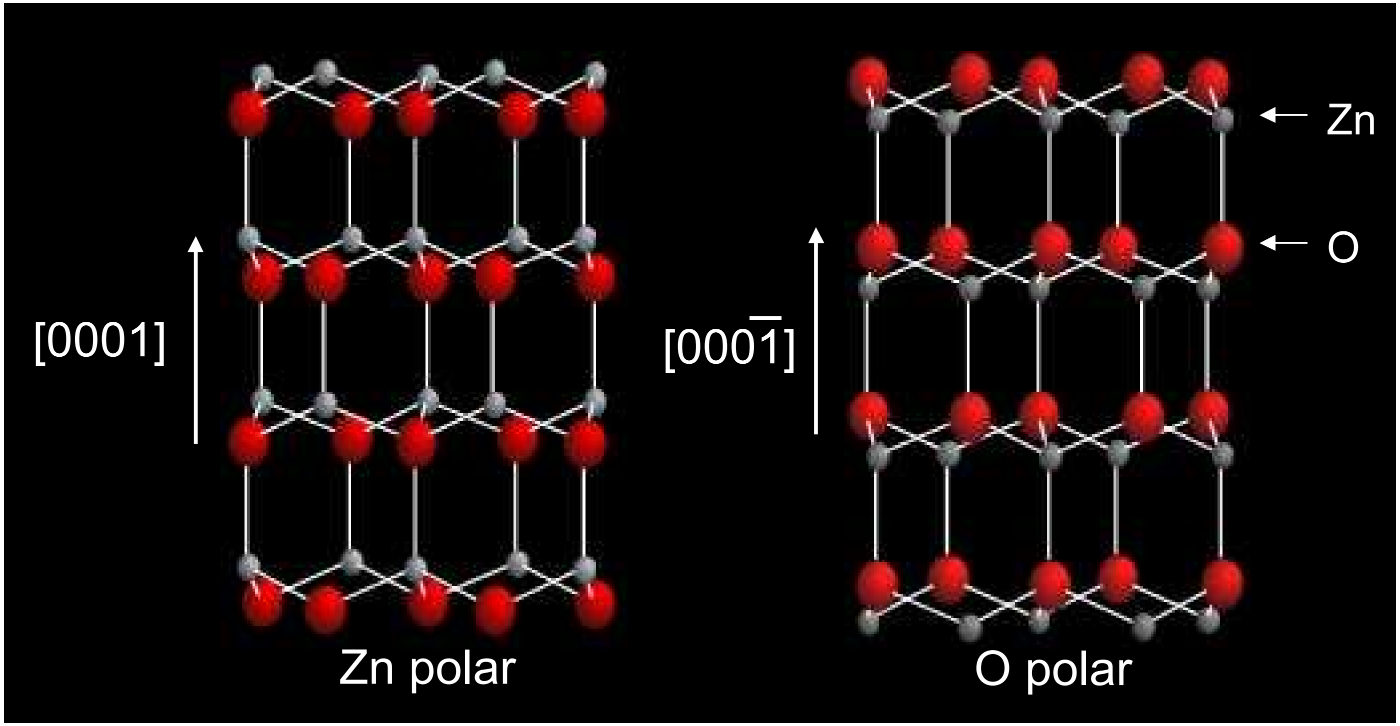
Which Side Up?



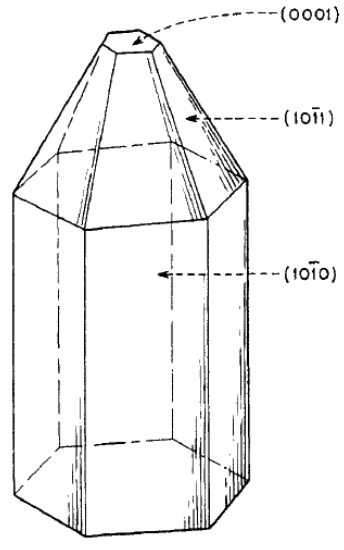
Why we care?

- Impurity incorporation
- Chemical resistance
- Piezoelectric response

- d_{33} is defined wrt to +c
- For ZnO, $d_{33} > 0$, i.e. crystal expands when electric field is in the +c direction

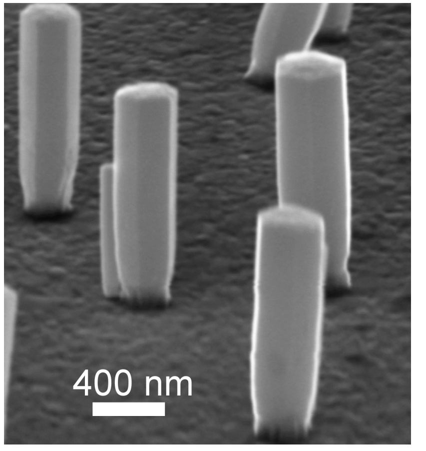
Can Morphology Tell Us Orientation?

Conventional



Laudise & Ballman, *J. Phys. Chem*, **64**, 688 (1960).

ZnO Nanorods on Ag



- Equilibrium shape; surface energy
- Based on crystal shape comparison, one might conclude that ZnO rods orient with [0001-] up on Ag
- The growth might not produce equilibrium shape; crystal morphology can be changed with organic modifier

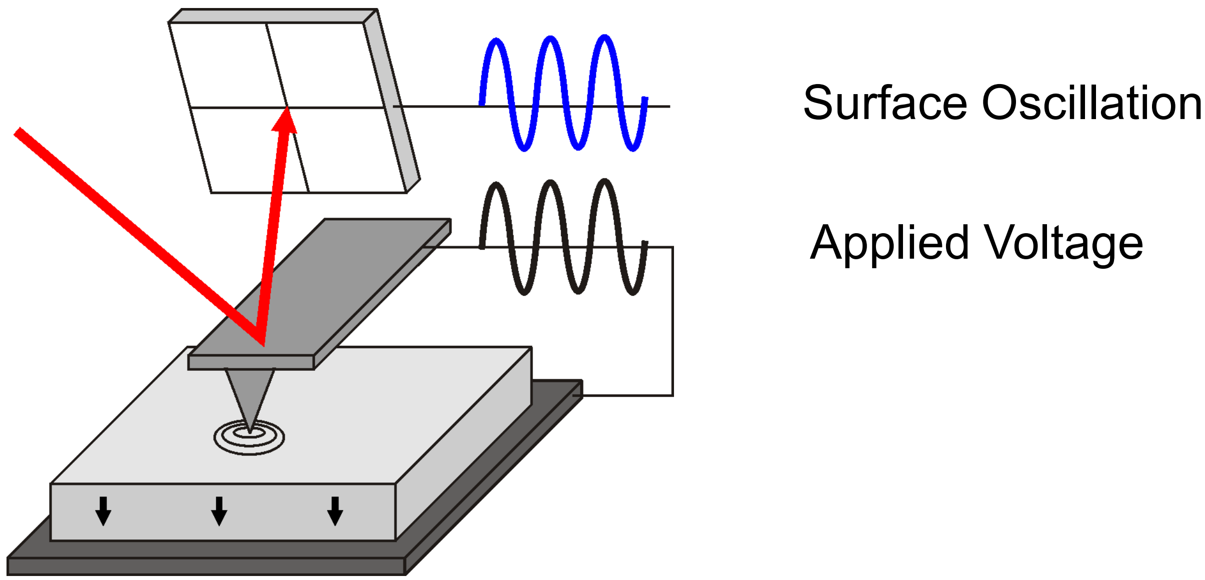
How Do We Tell?

Techniques available:

- Convergent beam electron diffraction
- Coaxial impact collision ion scattering spectroscopy
- Anomalous dispersive XRD
- Piezoelectric Force Microscopy (PFM)

Our approach:

- PFM
- Well-characterized Single Crystal ZnO reference (Tokyo-Denpa)



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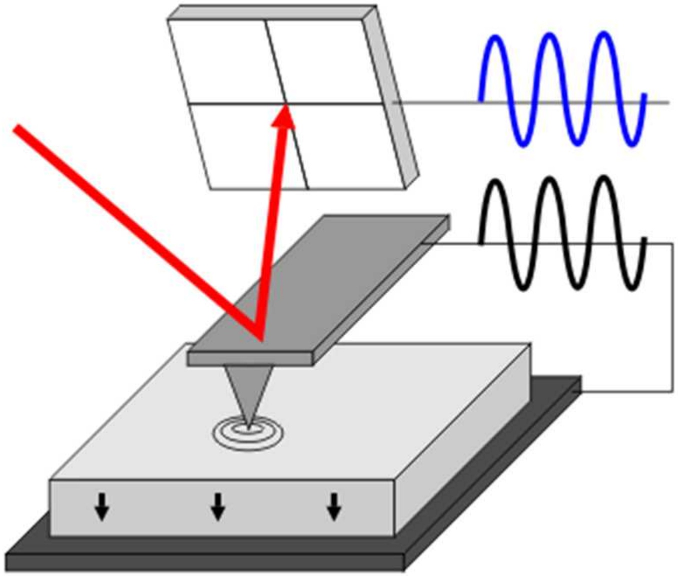
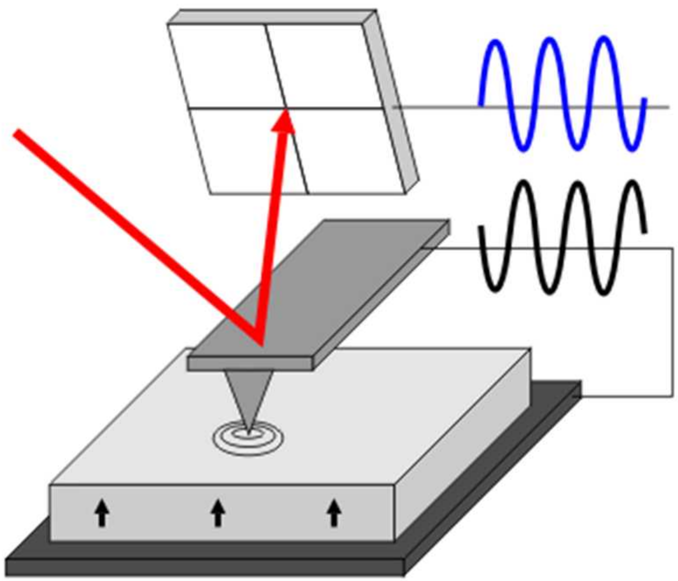
Piezoelectric Force Microscopy



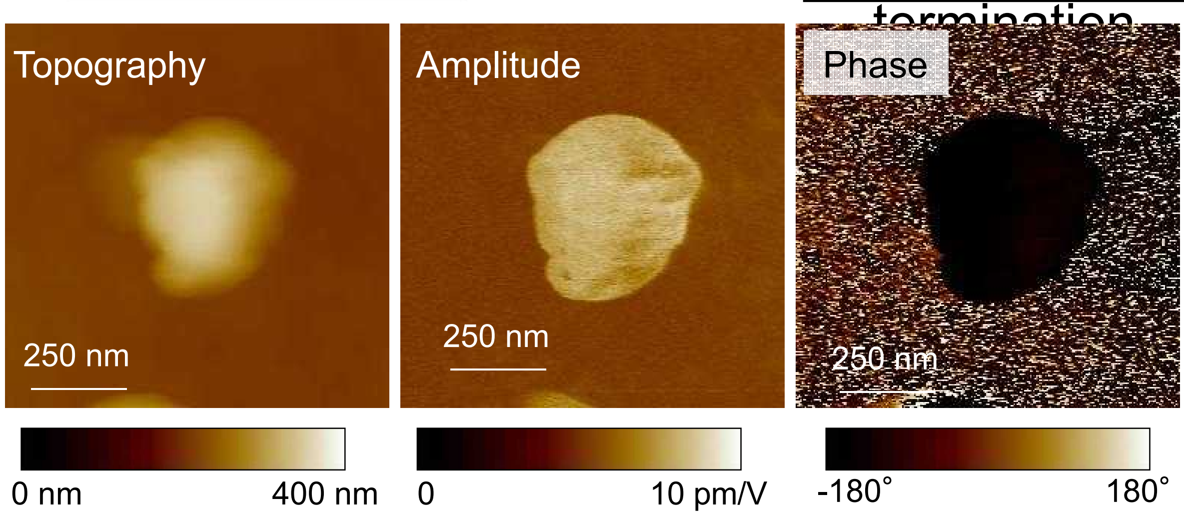
Surface Oscillation

Applied Voltage

Piezoelectric Force Microscopy



- The phase relationship between the electric field and the piezoelectric response depends on the crystal orientation:
  - (0001-): 0° , in phase
  - (0001): 180° , out of phase
- Bulk property, not surface termination



Scrymgeour, JAP 101, 014316 (2007)

Phase = -180° ➡ ZnO grows on Ag in [0001]

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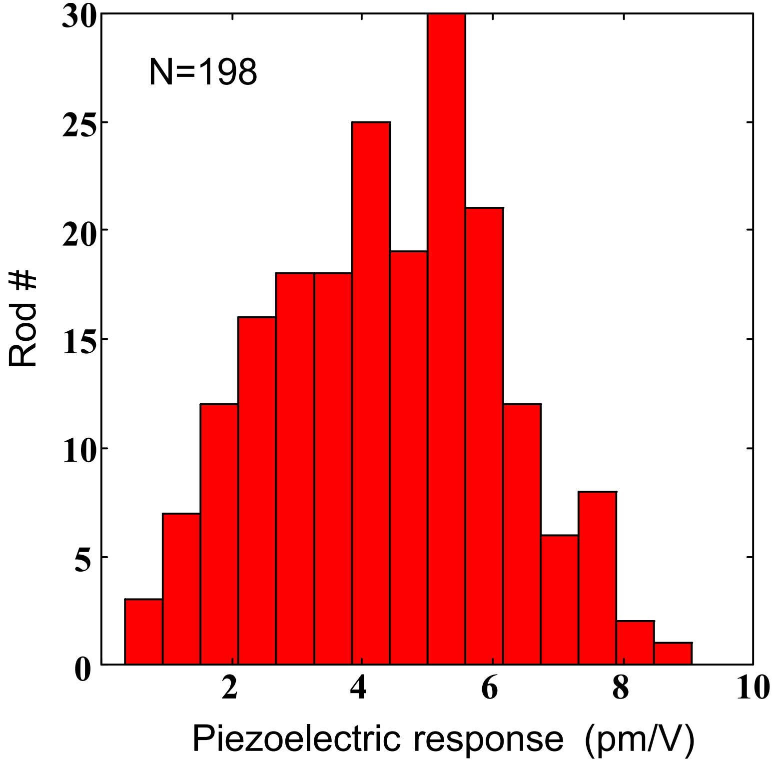
JAP 101, 014316 (2007)

Piezoelectric Coefficient

Amplitude Histogram

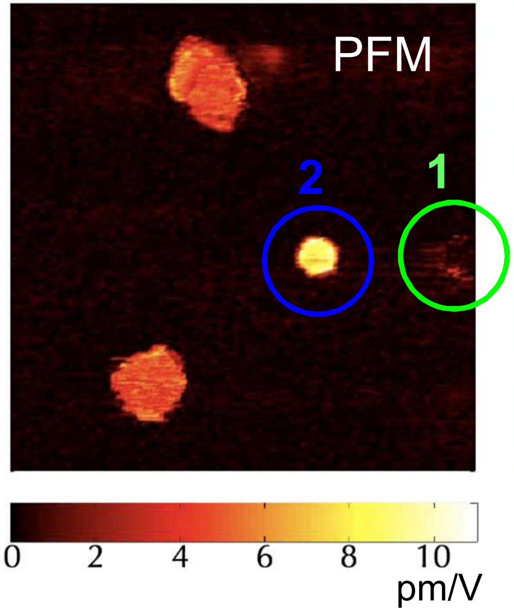


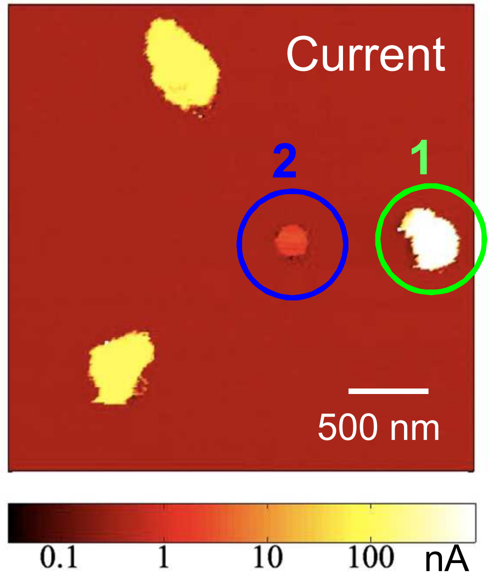
Frequency Independent Amplitudes

	Response (pm/V)
Bare Quartz	0.8 ± 0.06
Bare ZnO +z Face	2.97 ± 0.57
ZnO Nanorods	4.41 ± 1.73
Bare $LiNbO_3$	7.11 ± 0.75

- Definite variation among different rods
  - Not correlated with diameter or height
  - A function of conductivity?
- Nanorods have responses ~1.5 times of single X'tal ZnO

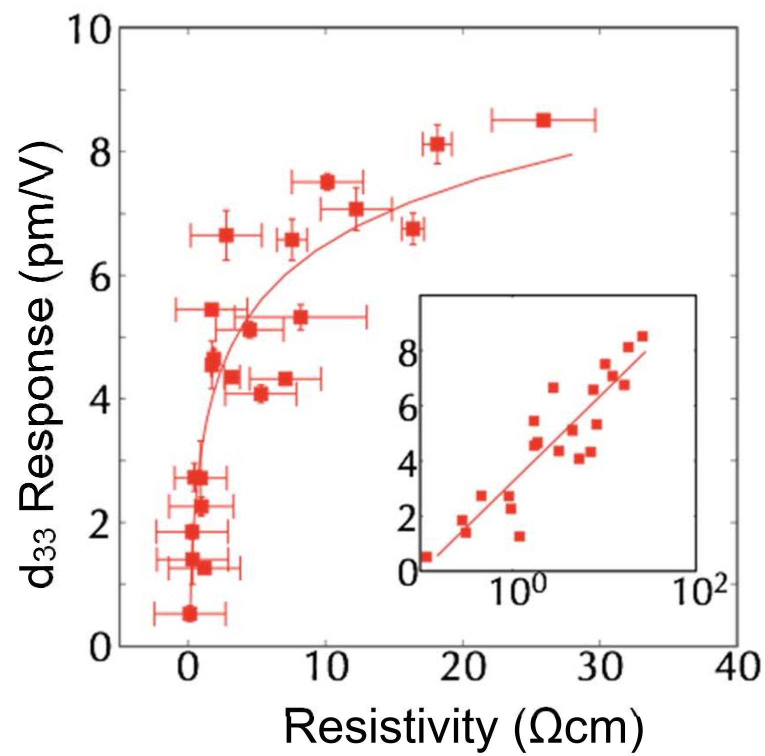
Corrleation between d_{33} and Conductivity

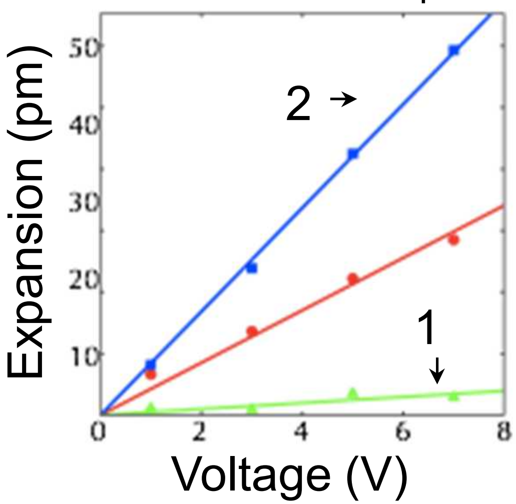


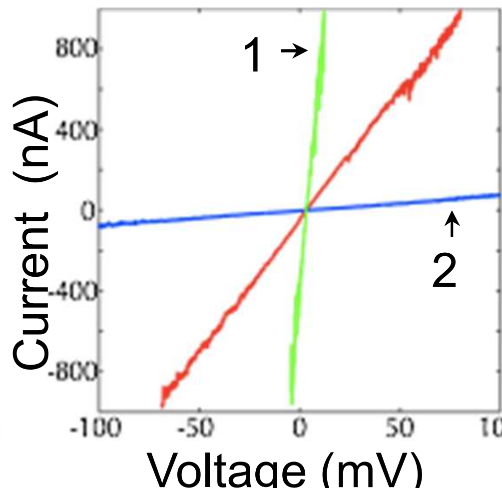


Low d_{33} ↔ High current

High d_{33} ↔ Low current







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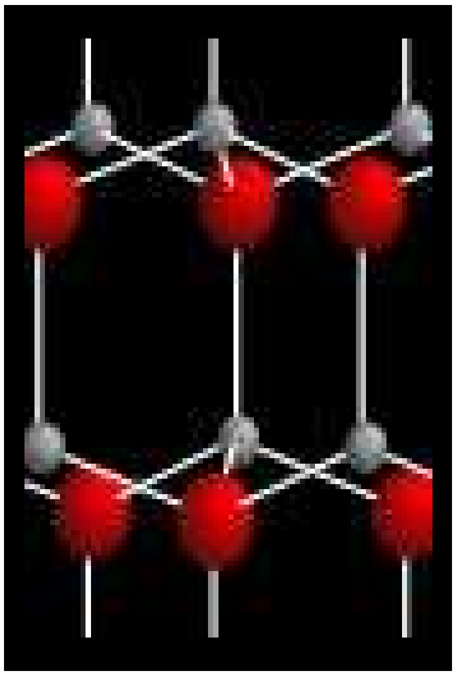
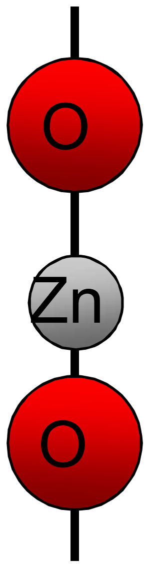
Madelung Constant Reduction

The Madelung energy is the bond strength in an ionic crystal





$$\alpha_M = e^{-k_s R_o} - \frac{1}{2} e^{-2k_s R_o} + \frac{1}{3} e^{-3k_s R_o} - \cdots$$

$$= 2 \ln[1 + e^{-k_s R_o}]$$

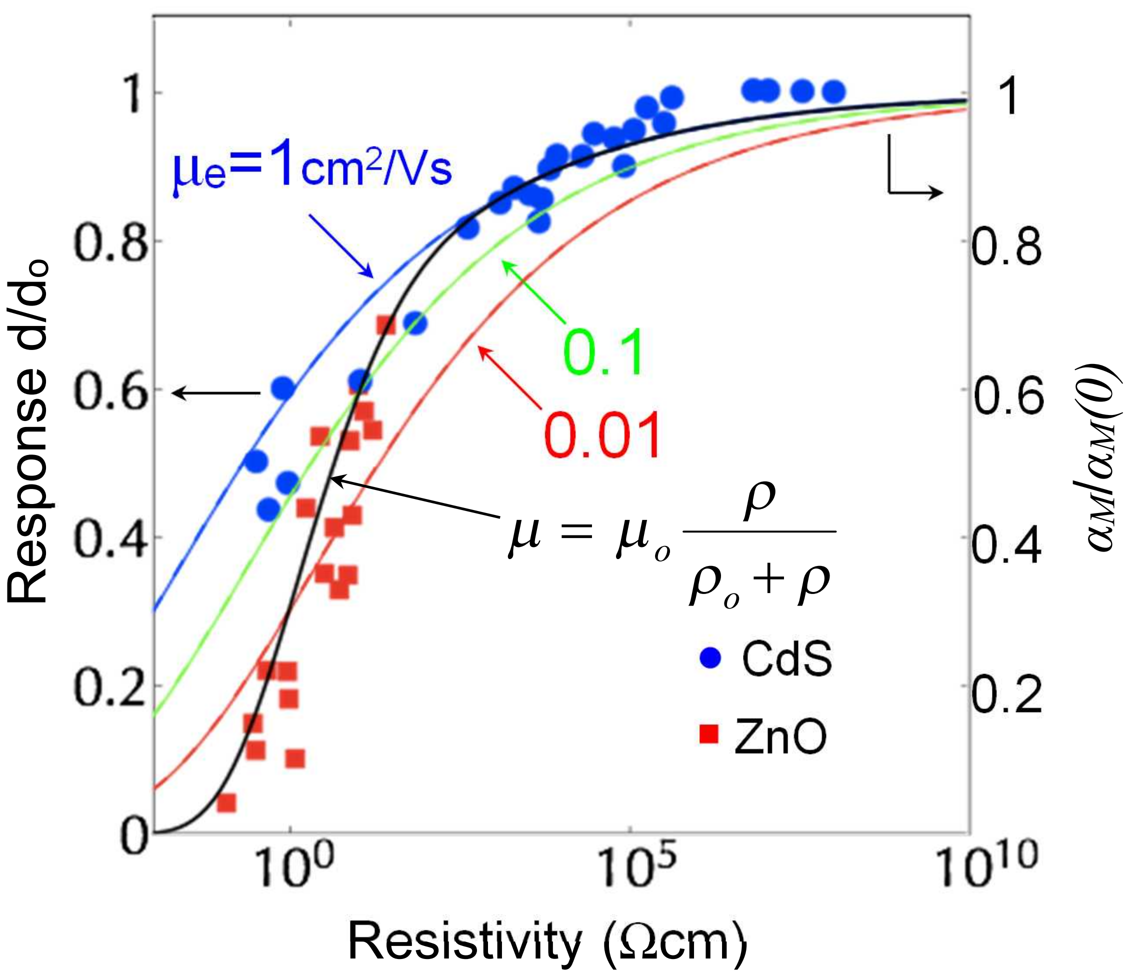
$$k_s = \sqrt{2} \left(\frac{3}{\pi} \right)^{1/6} \frac{n_c^{\;1/6}}{a_H^{\;1/2}}$$

→ Higher n_c, lower α_M

→ $\alpha_M(n_c) / \alpha_M(0)$

Ogawa, Oikawa, & Kojima,
JJAP, 10, 593 (1971)

Mobility Lowered as n_c *Increases*



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- Similar trend as CdS when normalized to saturation d_{33}
- Madelung constant reduction with constant μ_e does not match experimental results too well
- Must taking into account of mobility ↓ as n_c ↑ (defects and hence scattering centers ↑)
- Unintentional variations during growth lead to different nanorod properties

Summary

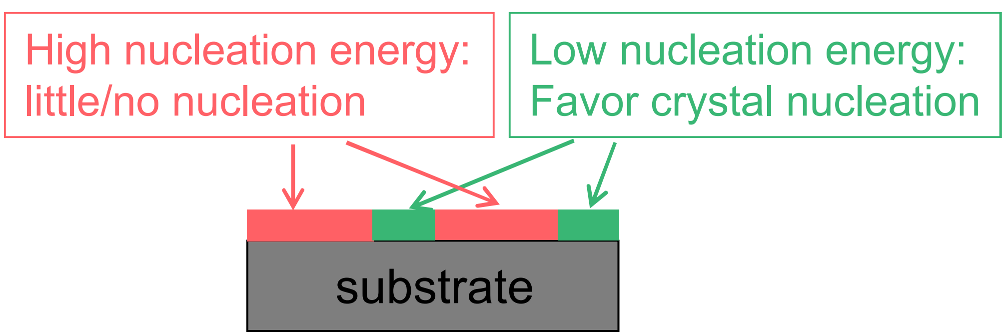
- Control placement of ZnO nanostructures on surfaces
  - Spatial placement, selectivity, crystal orientation, nucleation density
- ZnO nanorods grow “epitaxially” on Ag
  - Definite in-plane and out-of-plane crystallographic alignment:
    - ZnO $\langle 0001 \rangle$ || Ag $\langle 111 \rangle$
    - ZnO $\langle 11\underline{2}0 \rangle$ || Ag $\langle 1\underline{1}0 \rangle$
  - ZnO grows in the [0001] direction
- d_{33} and σ of individual nanorods are anti-correlated
  - Measure current and piezoelectric response on the same individual rods
  - Explain the d_{33} reduction with weakening of the ionic bond strength (Madelung constant)
  - Results indicate significant variations in defect/impurity incorporation during synthesis
- Current work
  - ZnO nanostructures as electron transporter in oxide-polymer solar cells

Experimental Approach

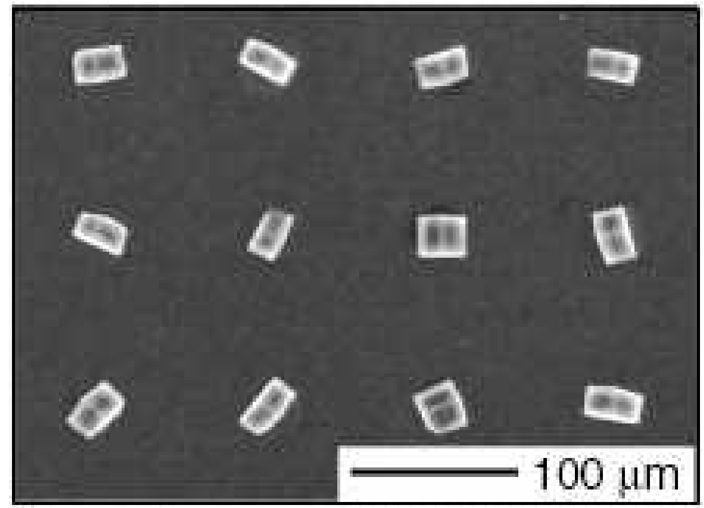
- Solution growth: low temperature (organic template/modifiers possible), environmentally benign, large area uniformity

  +

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



calcite

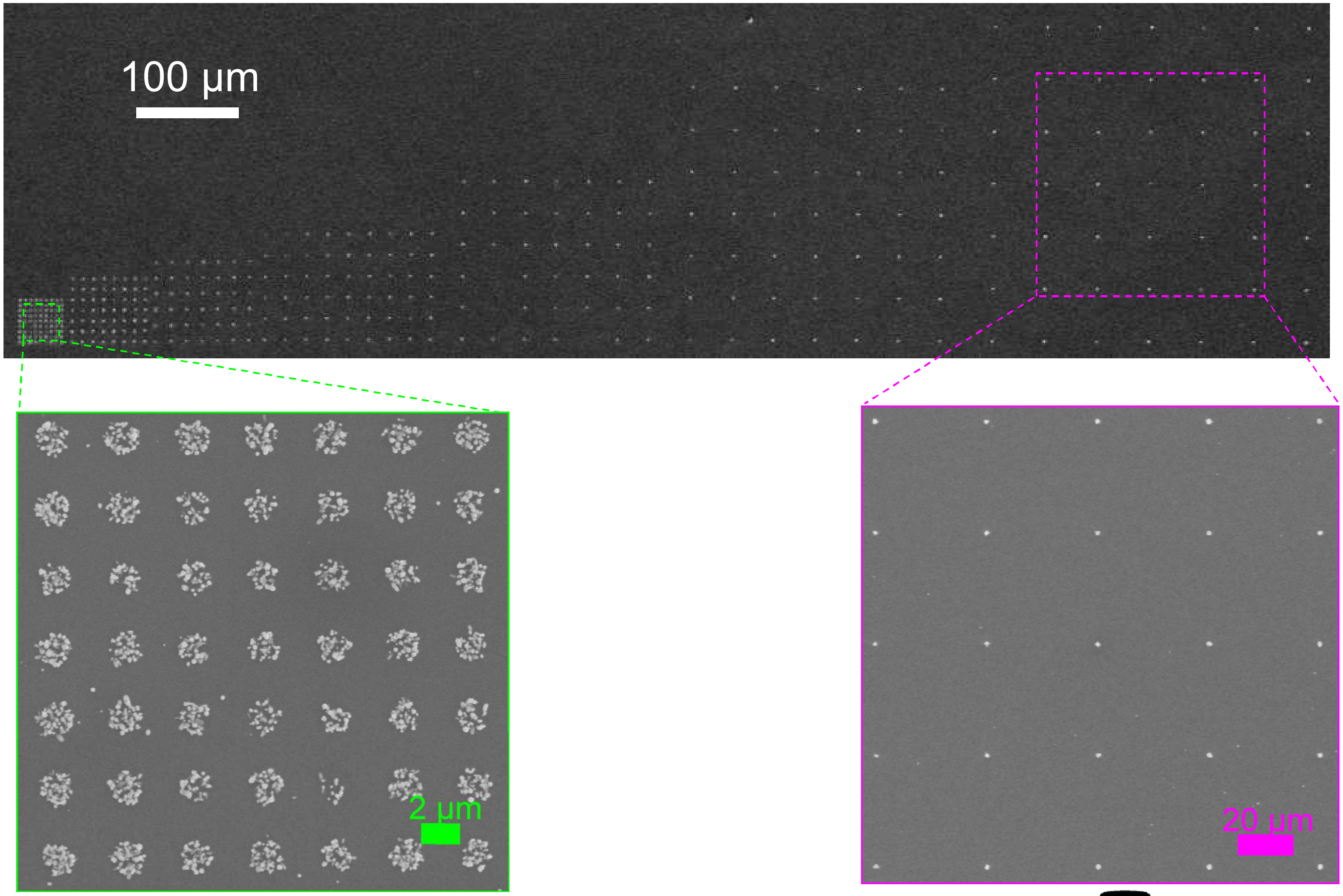


Aizenberg, Nature, 1999

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

Varying Average Density:

control active nucleation site density (N)

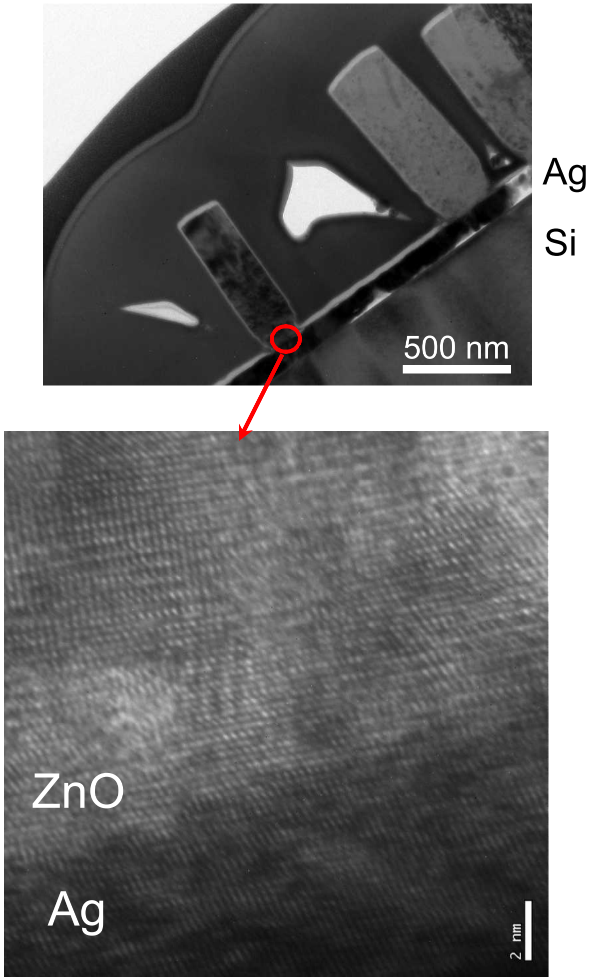


Sandia National Laboratories

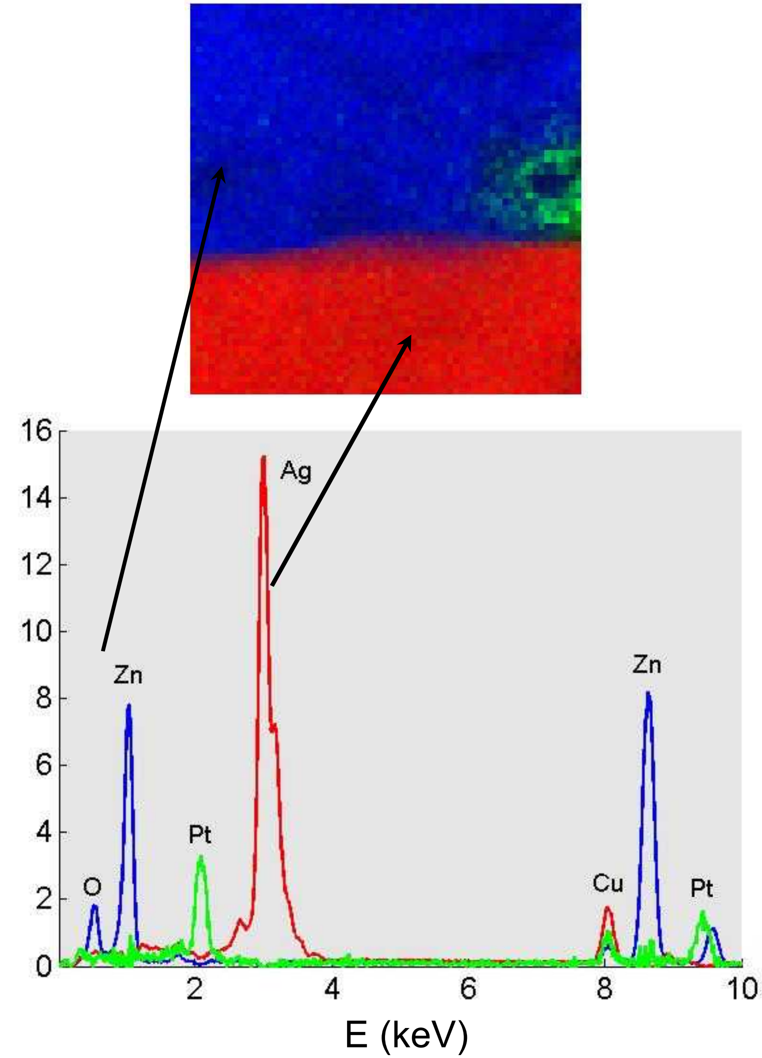
L. Brewer

TEM Study of ZnO-Ag Interface

High resolution



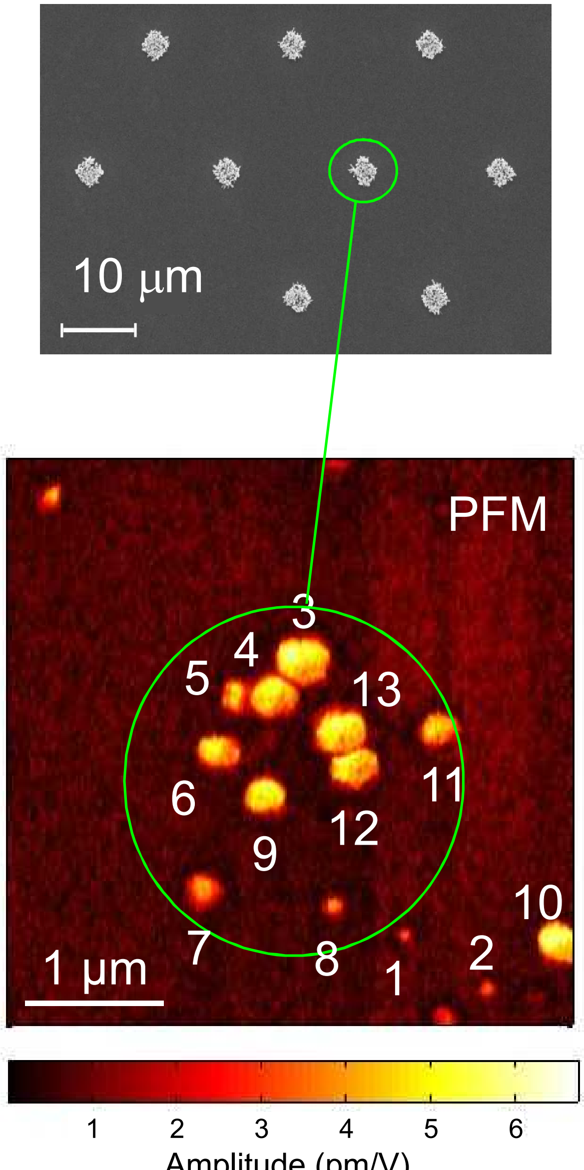
Chemical

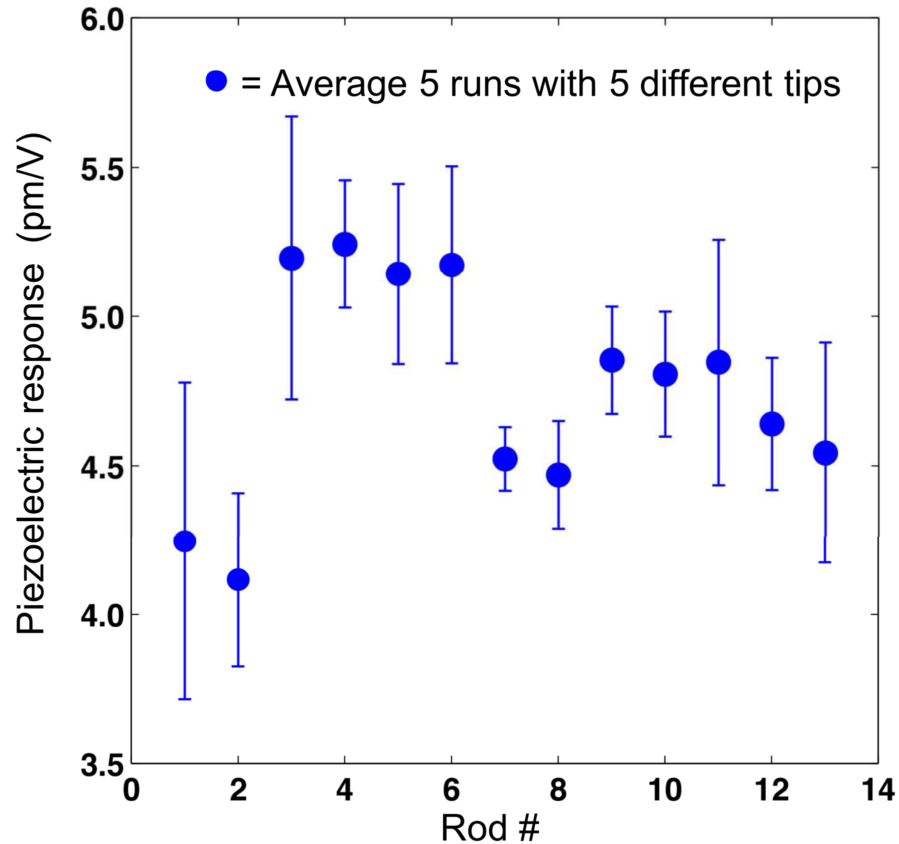


No "foreign" materials between ZnO & Ag; facetted interface. ZnO defected.

JAP 101, 014316 (2007)

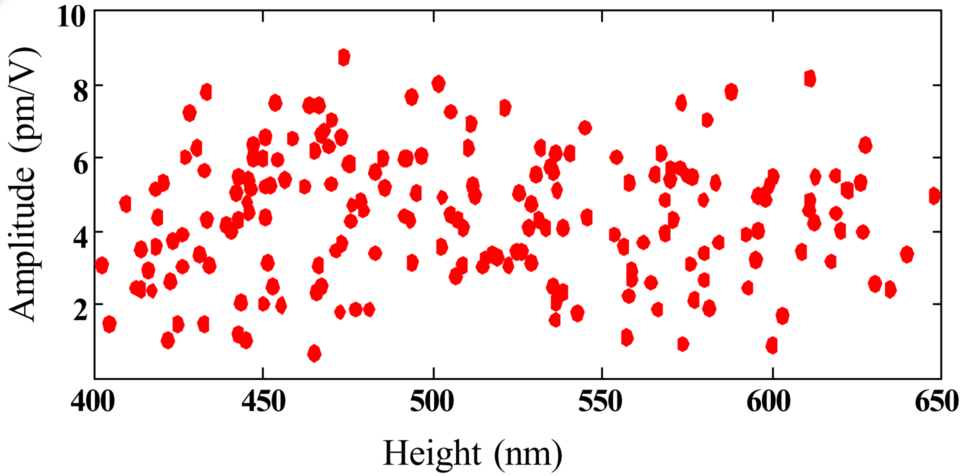
Repeatability

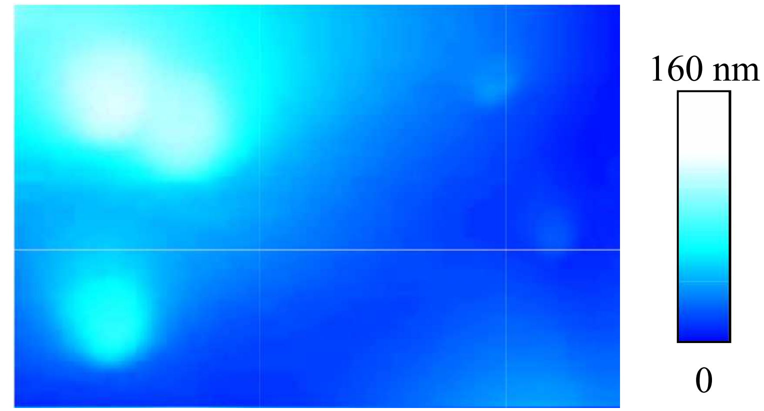


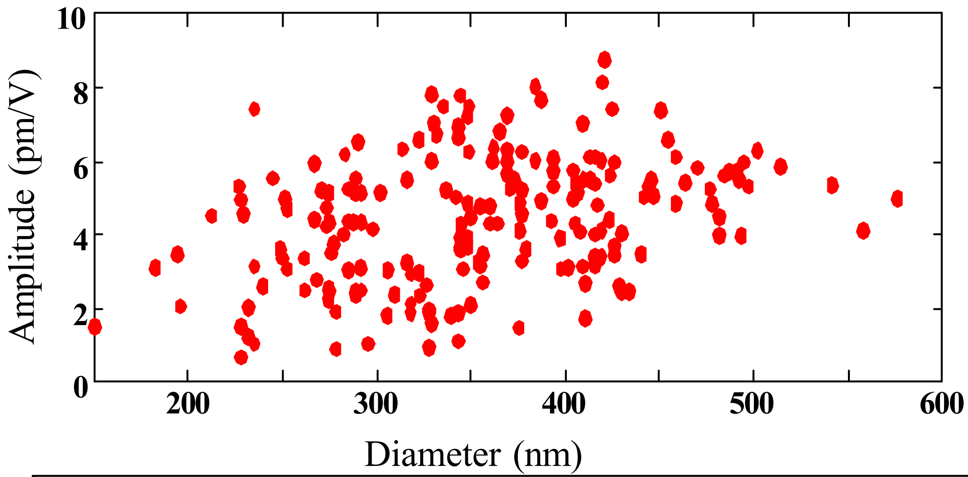


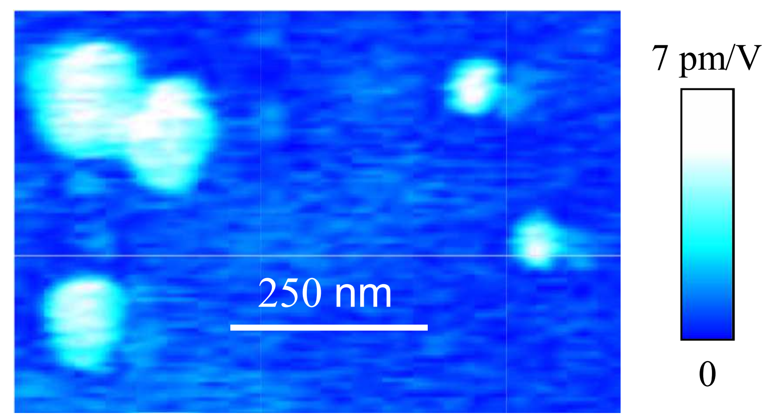
Easy to do because of the patterning

No Correlations with Size



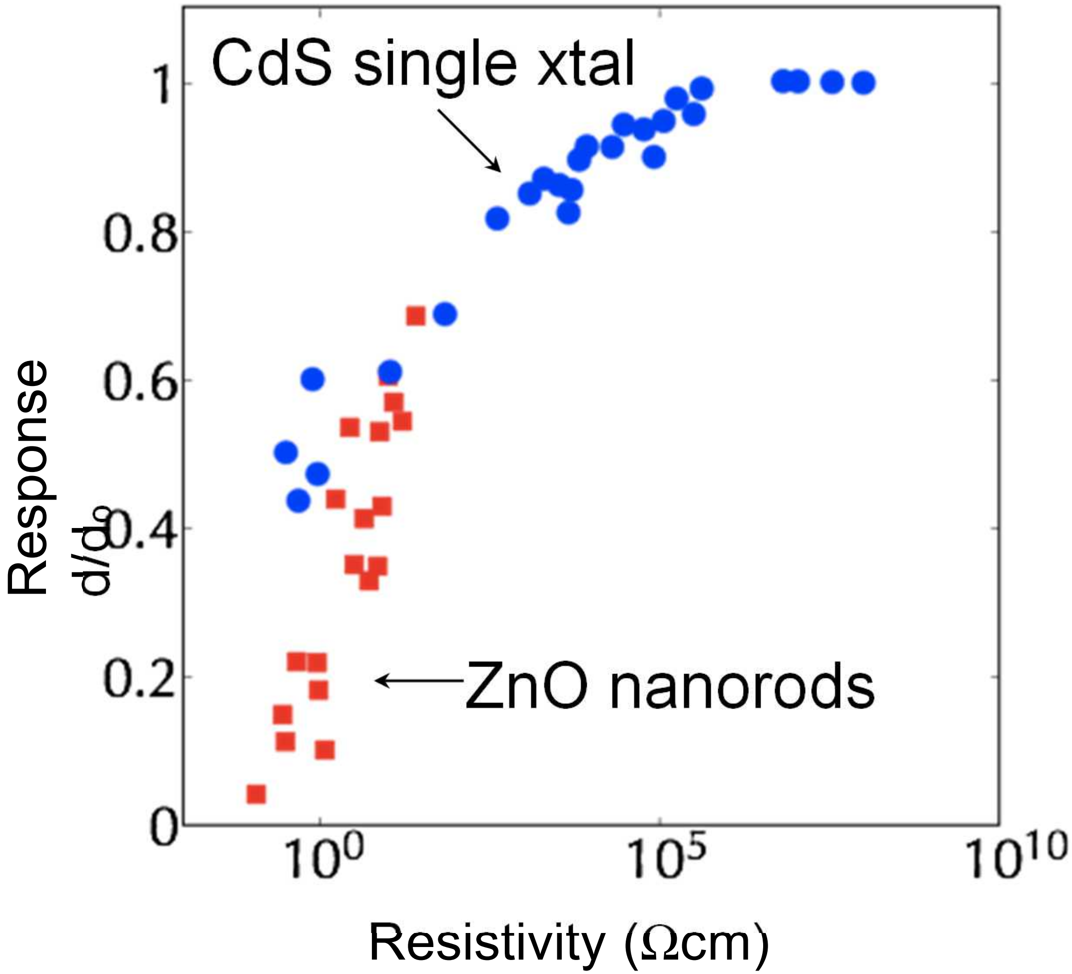






- Definite variation among different rods
  - Not correlated with diameter or height
  - A function of conductivity?

ZnO nanorod response similar to other piezoelectric semiconductors



Ohmic contacts prevent electric shielding.

Optical injection of carriers reducing d_{33} precludes structural defects.

CdS data from Ogawa, Oikawa, & Kojima, JJAP, 10, 593 (1971)