SAND2006-4835C

Piezoelectric and Electrical Properties of Solution Grown ZnO Nanorods

D. Scrymgeour, T. L. Sounart,
N.C. Simmons, J. W. P. Hsu

Electronic Materials Conference, June 28, 2006
Session A: ZnO Nanomaterials

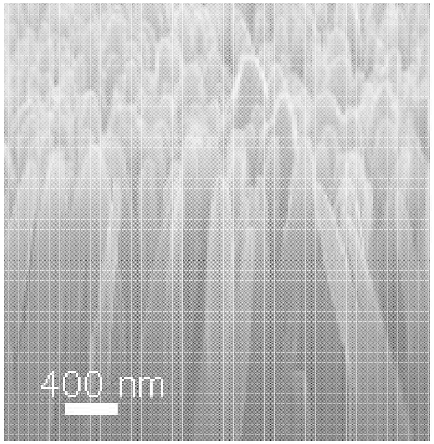
Acknowledgements:
D.C. Look (AFRL)
Sandia LDRD, Sandia Truman Fellowship

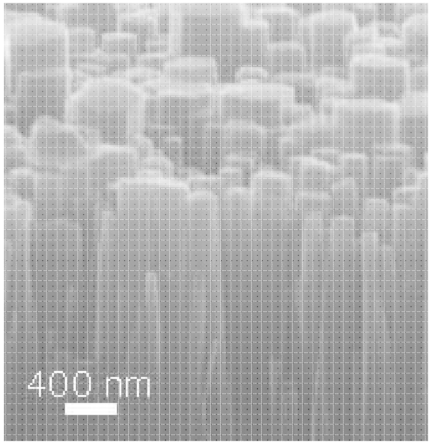
ZnO Nanostructures

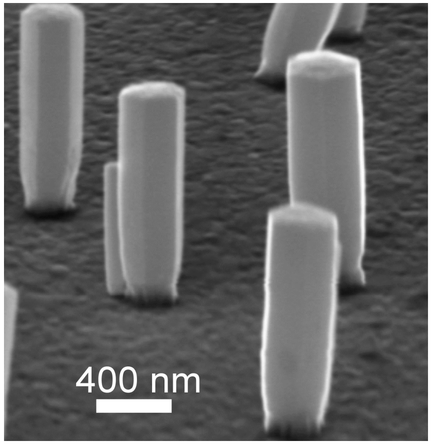
Wide bandgap semiconductor ($E_g \sim 3.4$ eV)
Interesting optical, piezoelectric, electrical transport
Several methods to grow nanostructures

Solution growth in water for 1-3 hours
on Ag coated Si

Z. R. Tian *et al* Nature Materials, 2, 821 (2003).
J.W.P Hsu *et al*, Nano Letters, 5, 83 (2005).



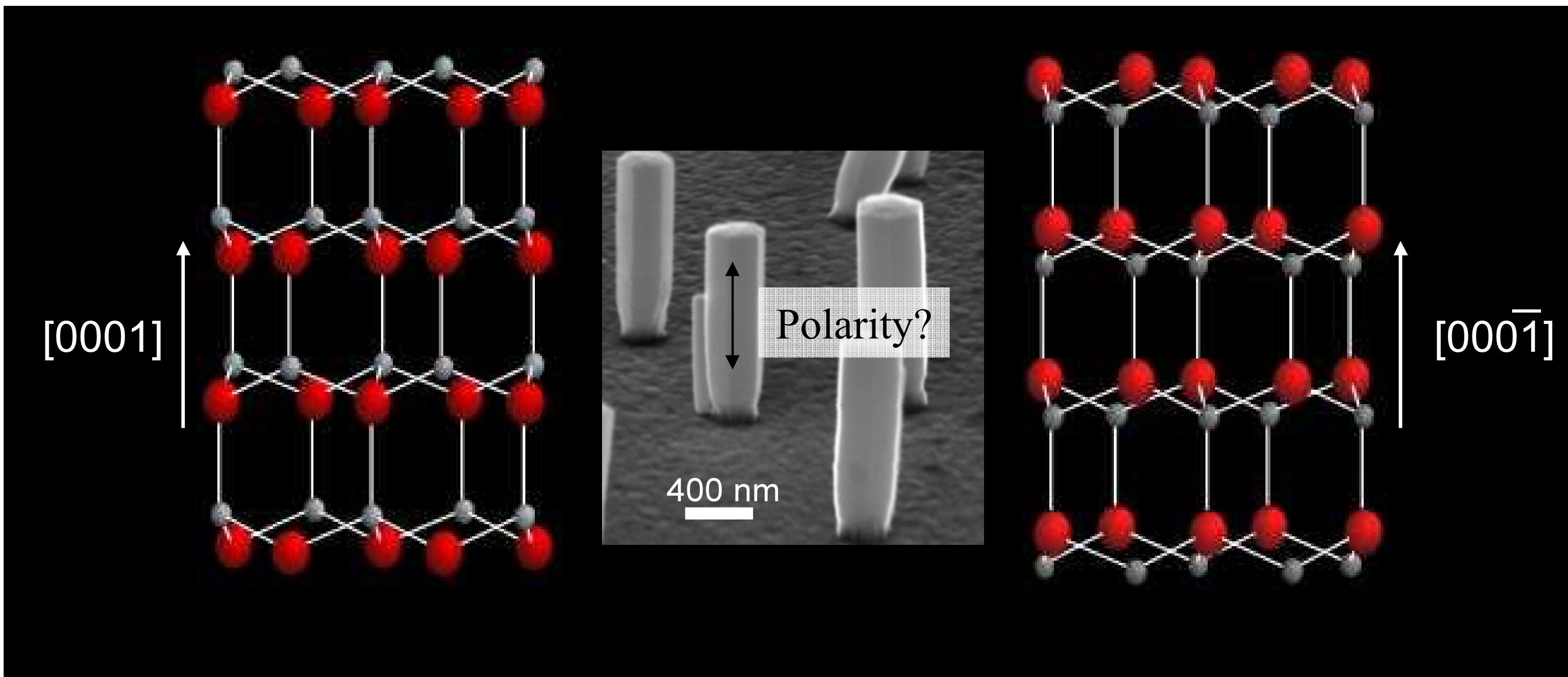




ZnO Crystal Structure

Crystal polarity ⟶ Defect incorporation, surface stability, piezoelectric, electric, optical properties

ZnO wurtzite structure $P6_3mc$ (6mm)



Sandia National Laboratories

Crystal polarity determination

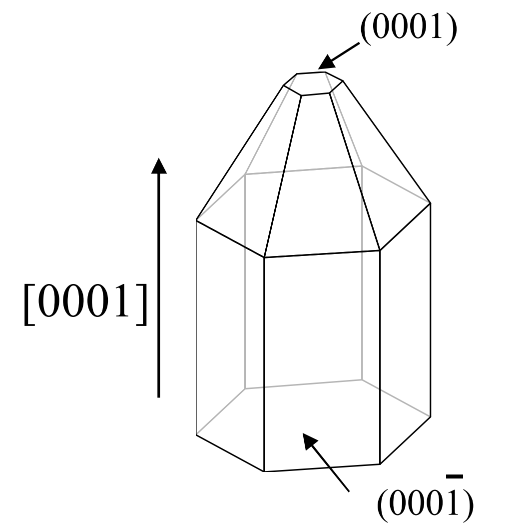
Increasing difficulty

- Morphology
- Etching
- Piezoelectric Effect
- Anomalous dispersion XRD
- Scanning Probes
- Coaxial impact ion spectroscopy
- Convergent Beam TEM
- Electron energy loss spectroscopy

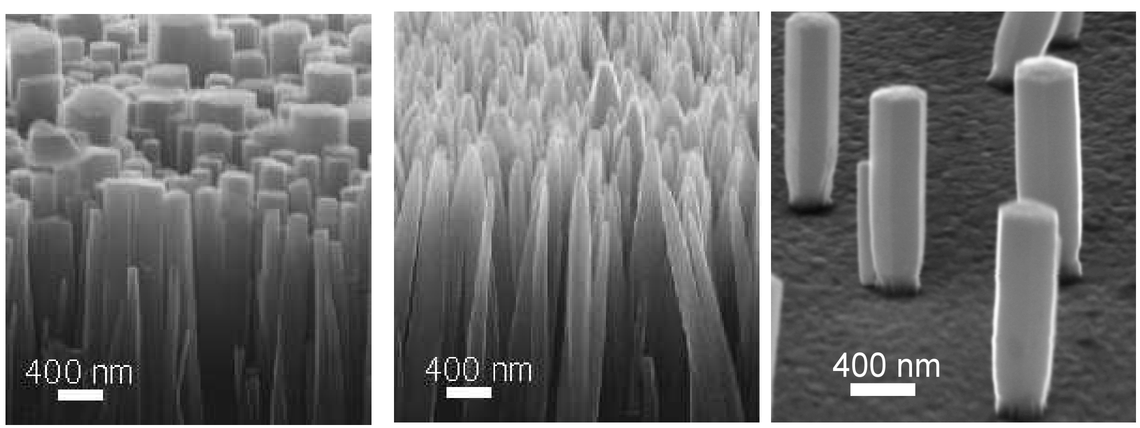
Crystal polarity determination

Increasing difficulty

- Morphology
- Etching
- Piezoelectric Effect
- Anomalous dispersion XRD
- Scanning Probes
- Coaxial impact ion spectroscopy
- Convergent Beam TEM
- Electron energy loss spectroscopy



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



Sandia National Laboratories

Crystal polarity determination

Morphology
Etching
Piezoelectric Effect
Anomalous dispersion XRD
Scanning Probes
Coaxial impact ion spectroscopy
Convergent Beam TEM
Electron energy loss spectroscopy

Piezoelectric Force Microscopy

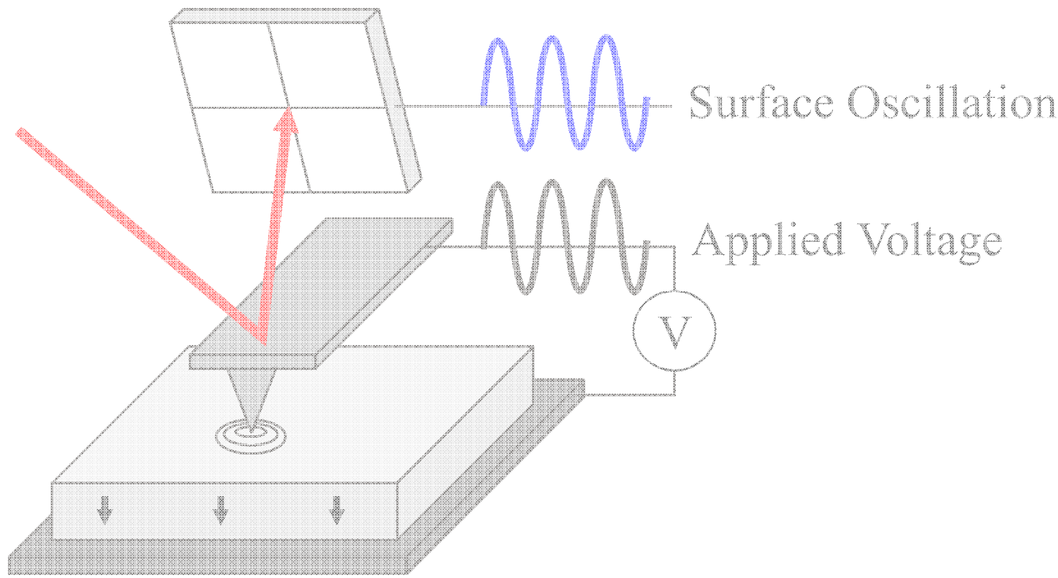
Piezoelectric Force Microscopy

Piezoelectric effect

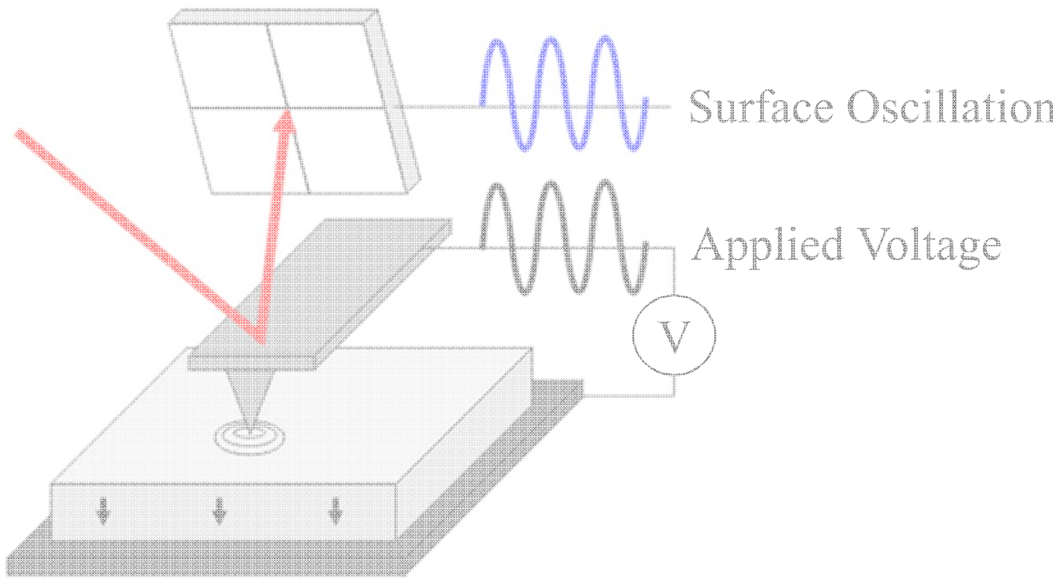
$$\varepsilon_3 = (d_{33})(E_3)$$

$$+\varepsilon_3 = (d_{33})(+E_3)$$

$$-\varepsilon_3 = (d_{33})(-E_3)$$



Piezoelectric Force Microscopy



Topographic Data

+

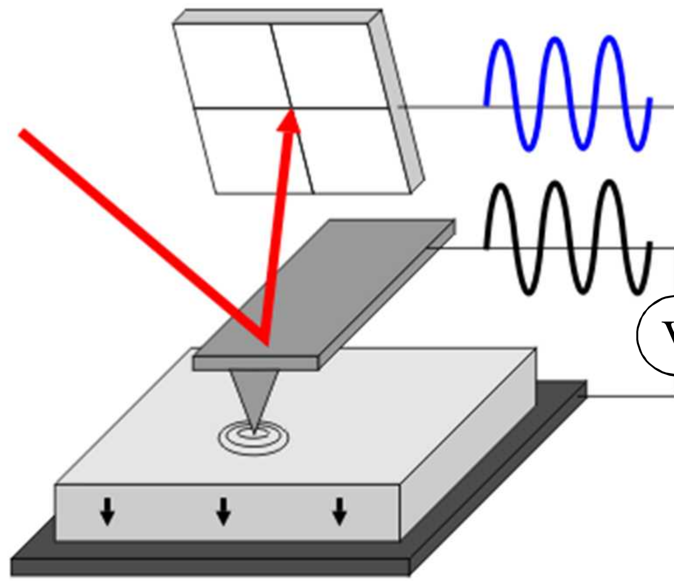
Piezoelectric Data

Spatial variation :

- Amplitude → Strength of piezoelectric response (d_{33})
- Phase

Piezoelectric Force Microscopy

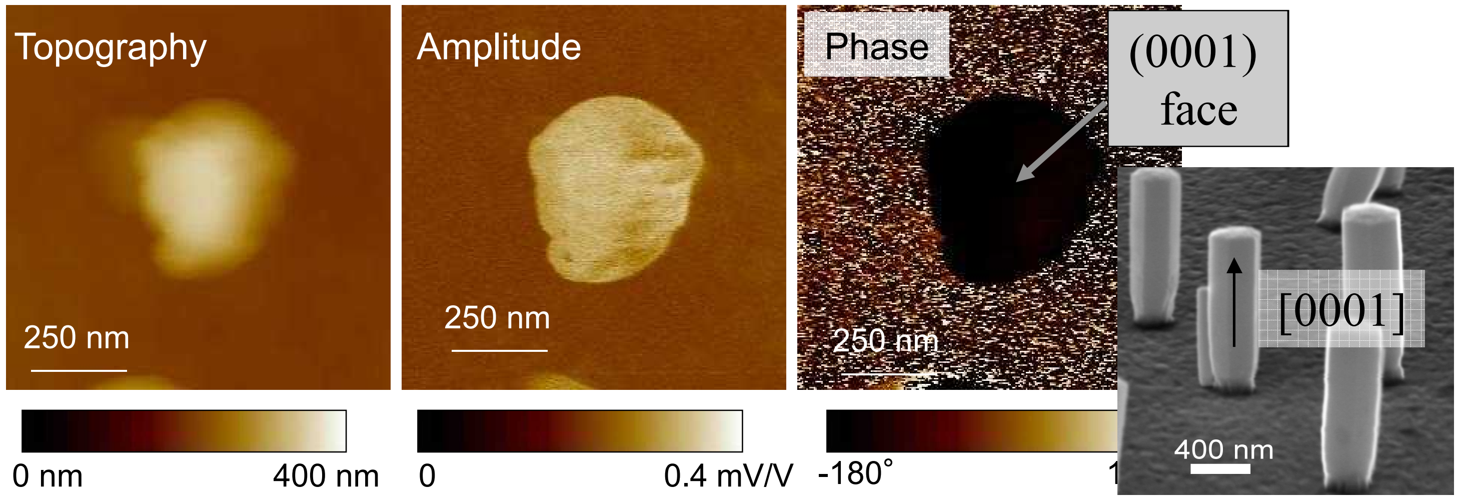
Topographic Data
+
Piezoelectric Data

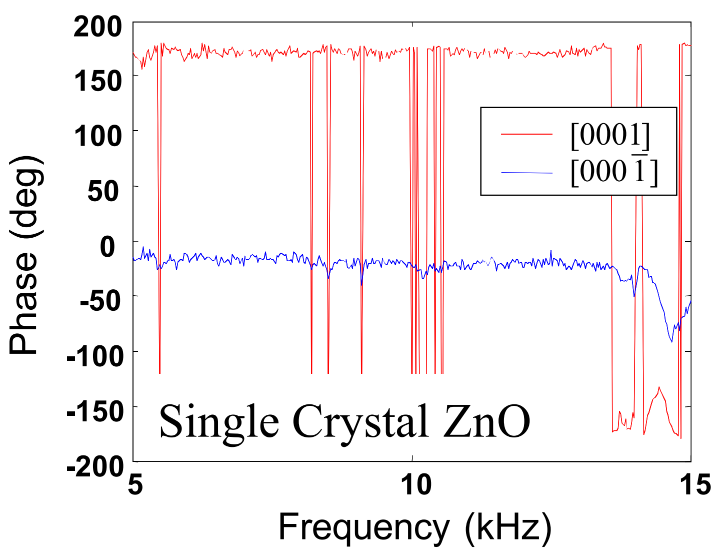


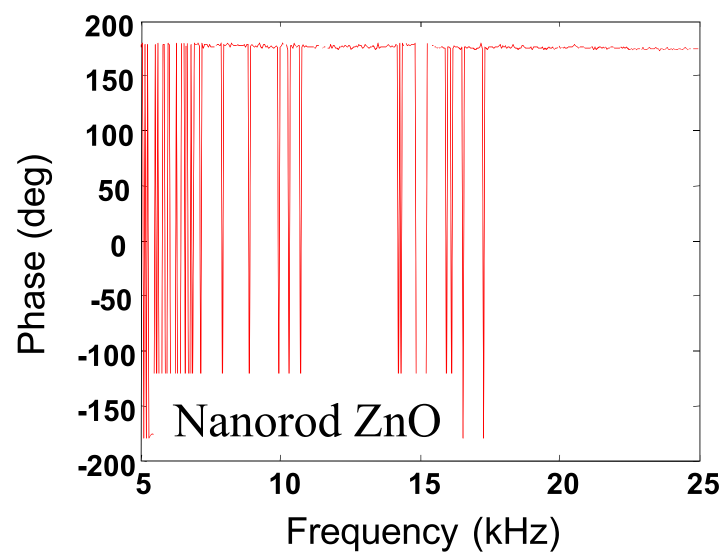
Spatial variation :
- Amplitude
- Phase → [0001] face = **In phase** with AC voltage

[$000\bar{1}$] face = **Out of phase** with AC voltage

Nanorod Orientation





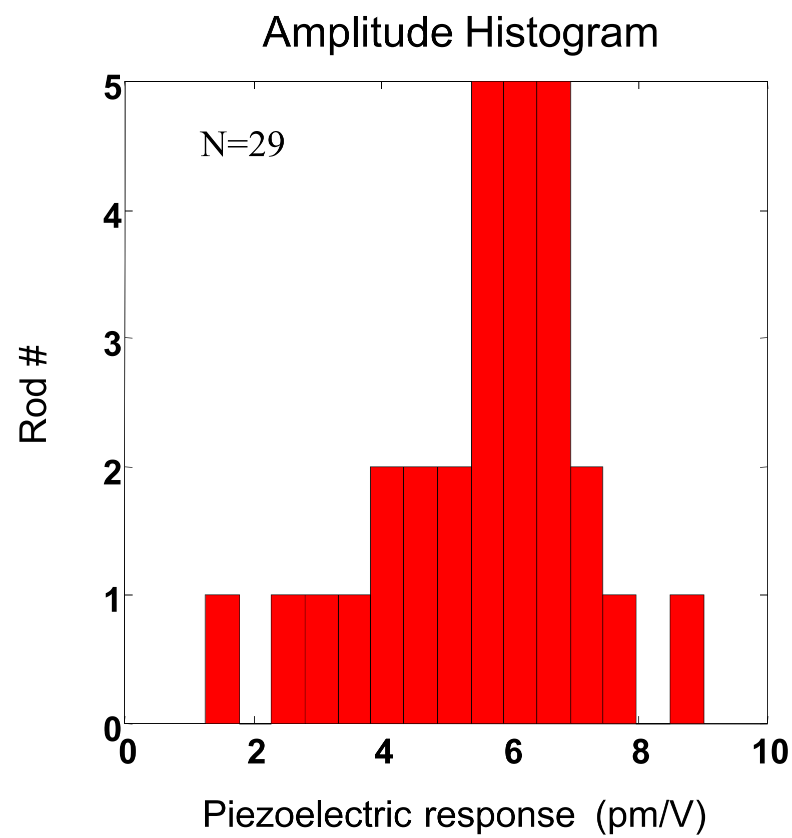


Piezoelectric Response (d_{33})

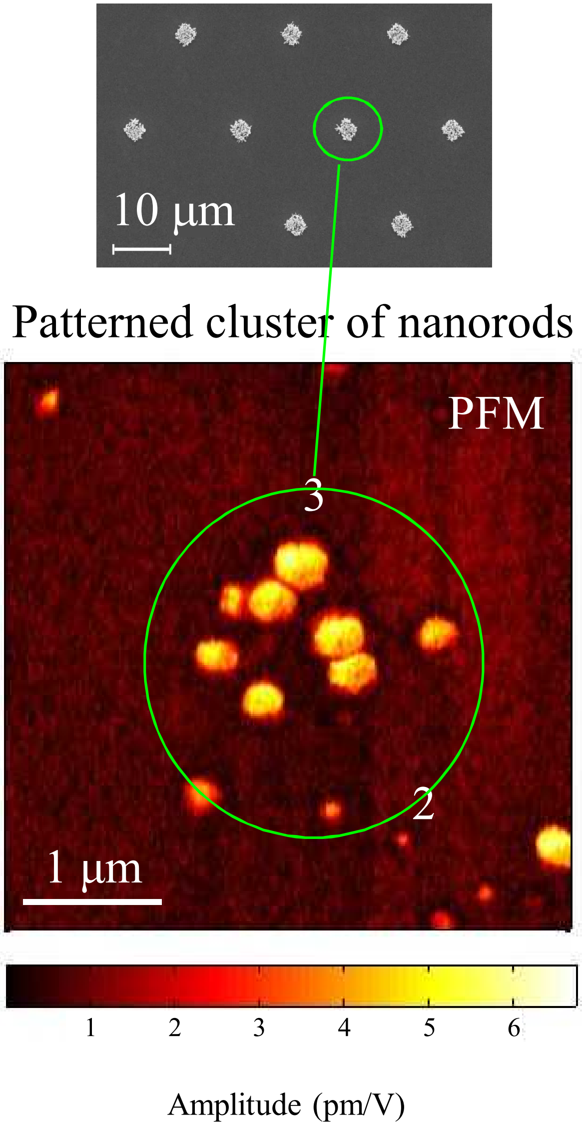
Amplitude Response

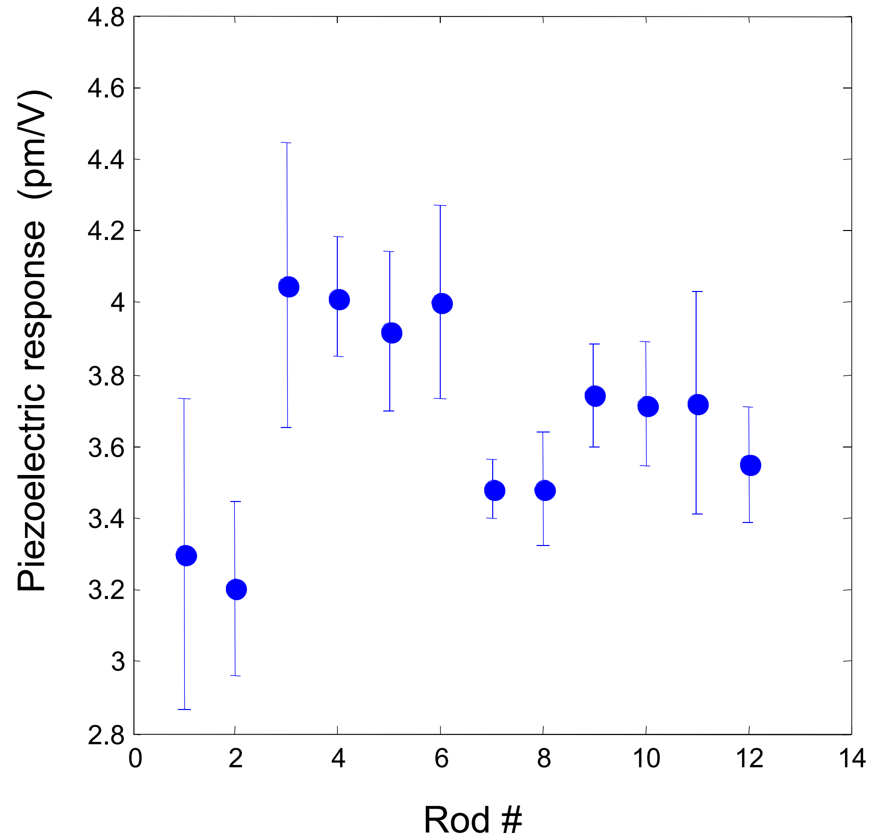
	Response (pm/V)	Ratio
Bare ZnO +z face	**2.97 ± 0.57**	
Nanorods	**5.61 ± 1.61**	**1.9**
$LiNbO_3$	**7.17 ± 0.76**	

Zhao *et al*, Nanoletters, 4, 587 (2004).

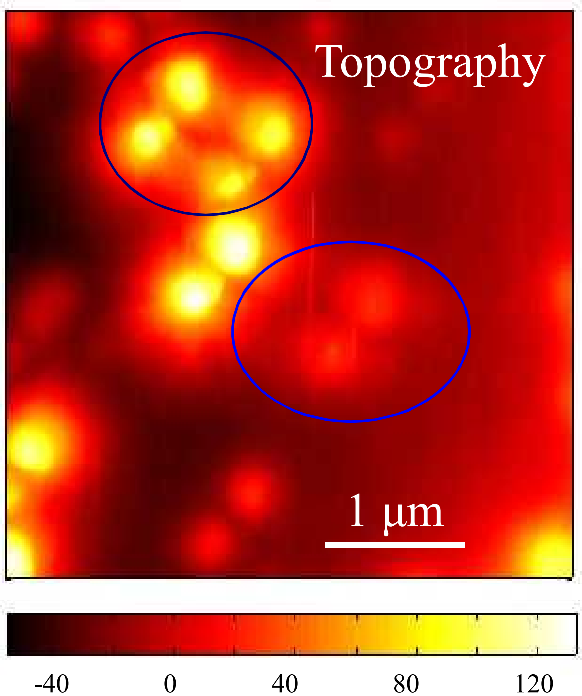


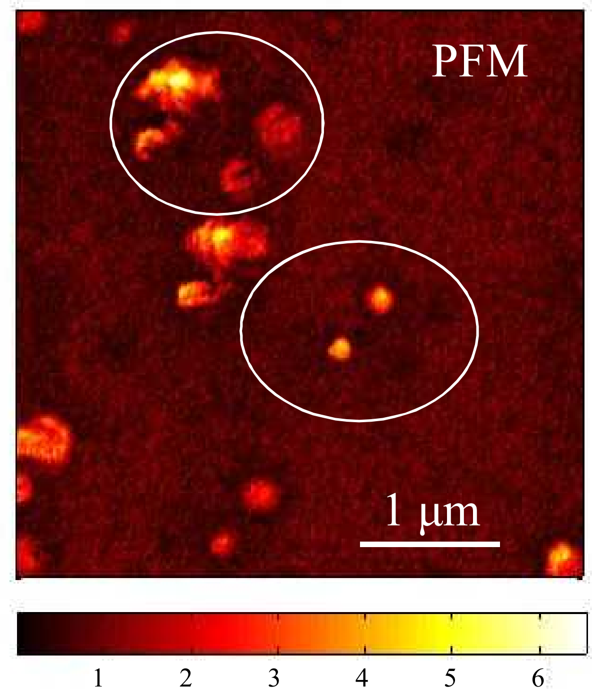
Reproducibility of Measurements





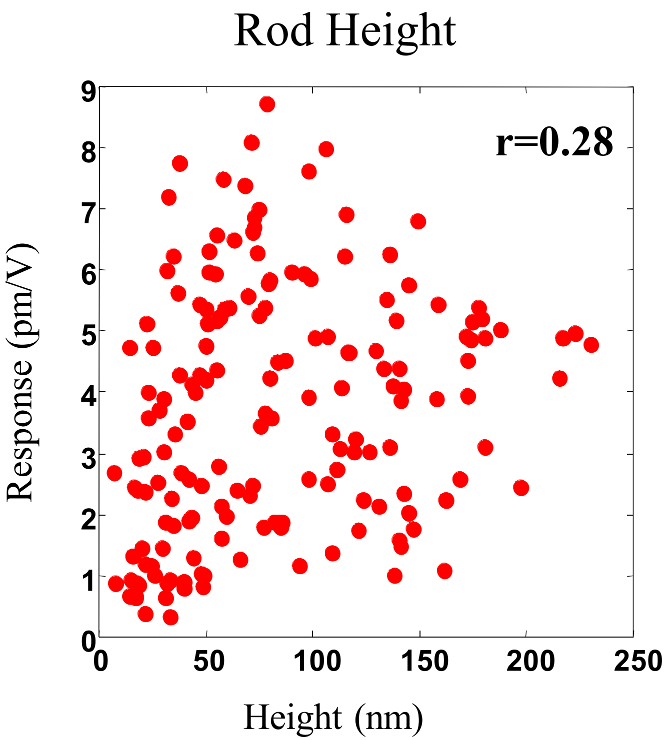
Variability of Response

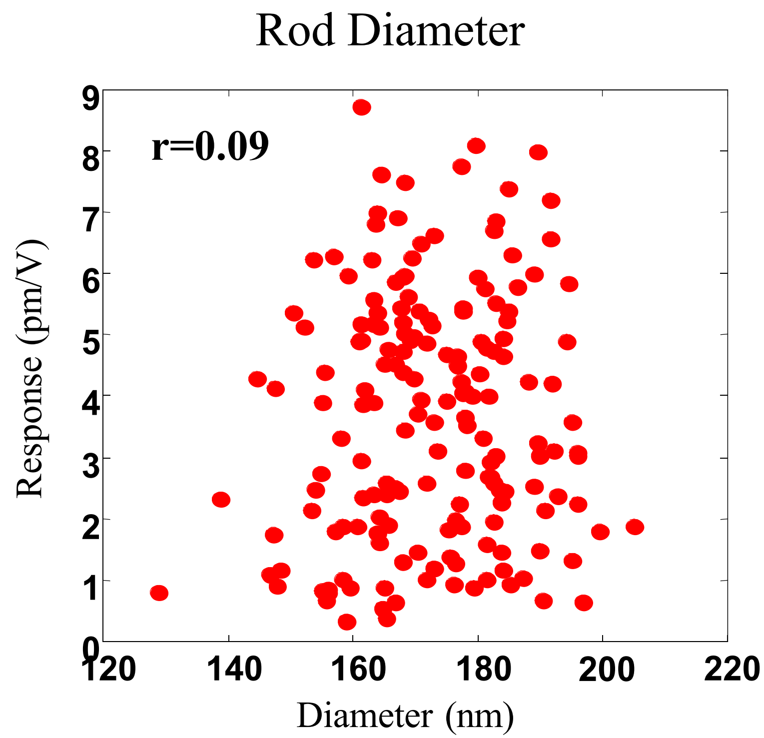




No clear correlation to height

Correlations

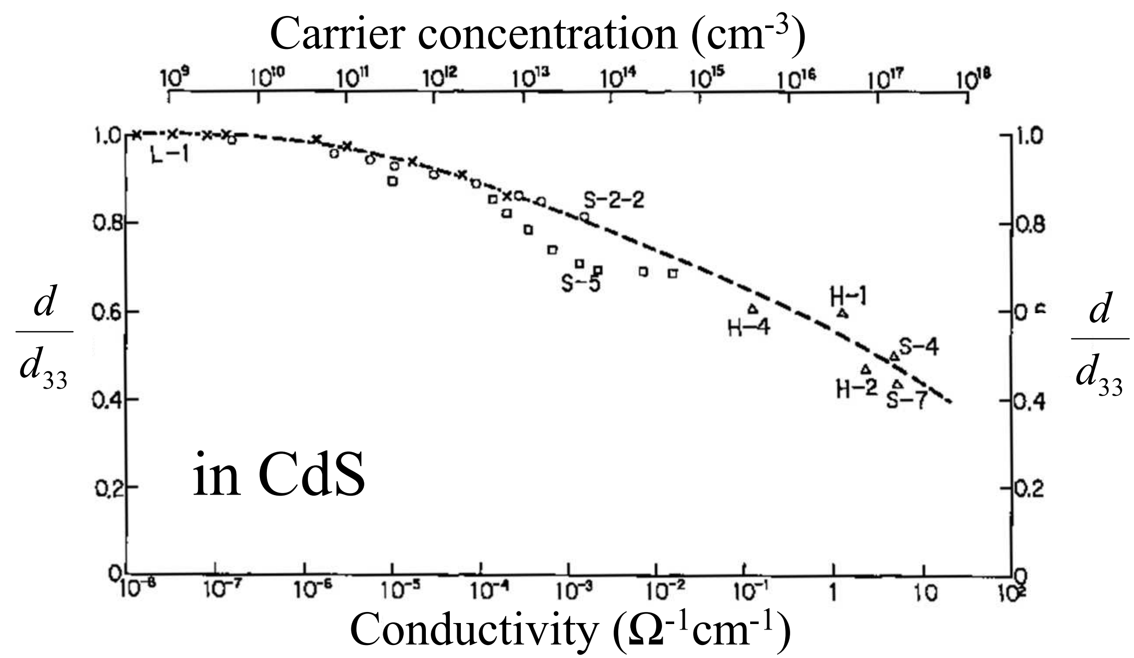




- Measurements repeatable within same field of view
- Variation not correlated with the physical dimensions

Electrical Properties

Intrinsic n-type semiconductor

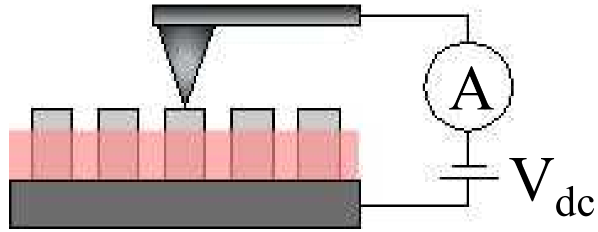


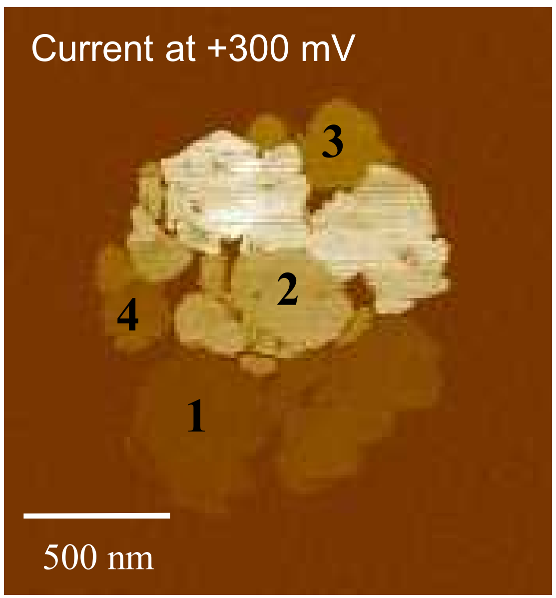
From Ogawa et al. JJAP, 10, 593, (1971).

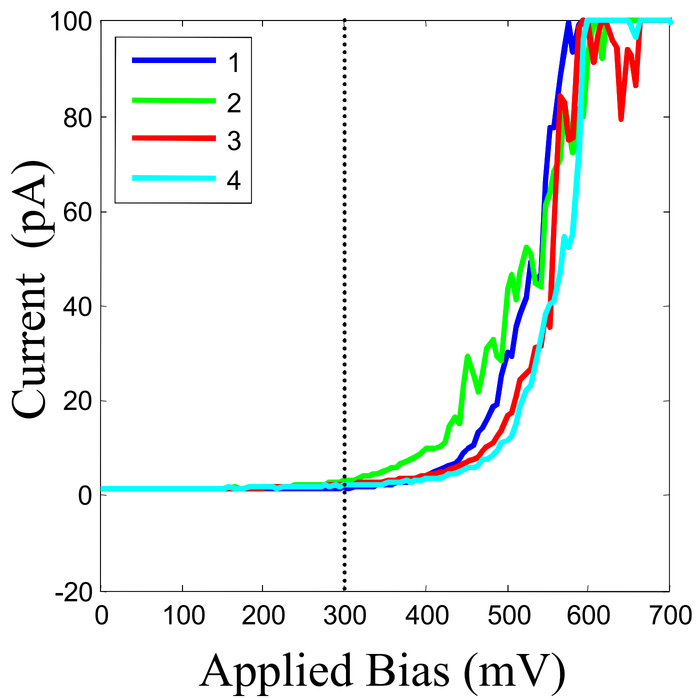
ZnO d_{33} = 12.4 pm/V ⟶ Li doped ZnO

Crisler, Proc. IEEE, 56, (1968)
Tokarev *et al*, Sov. Phys. Solid State, 17, (1975)

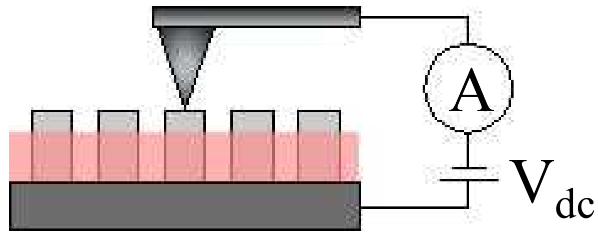
I-V Curves using C-AFM

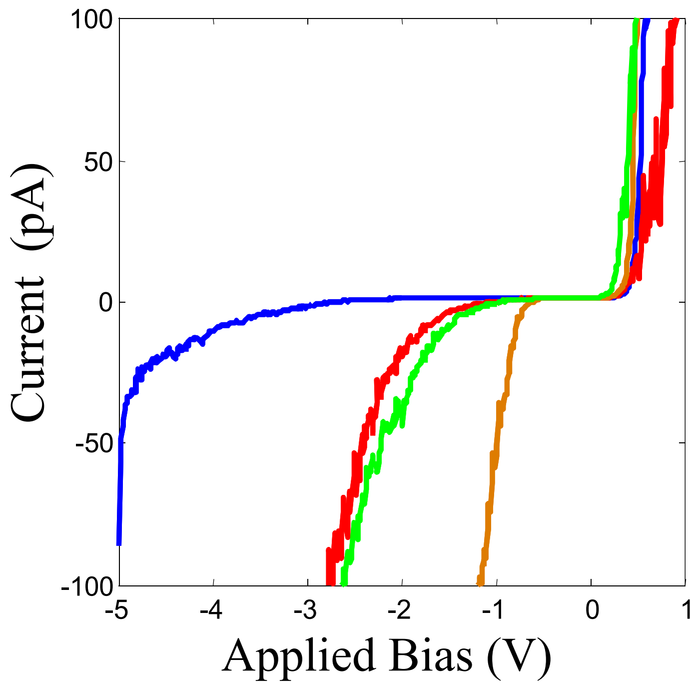






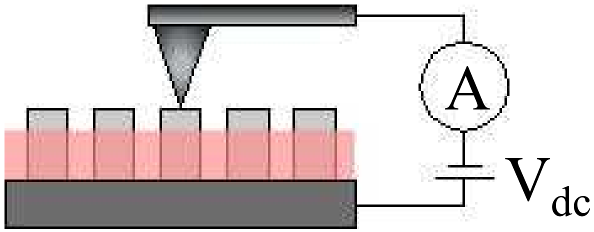
I-V Curves using C-AFM

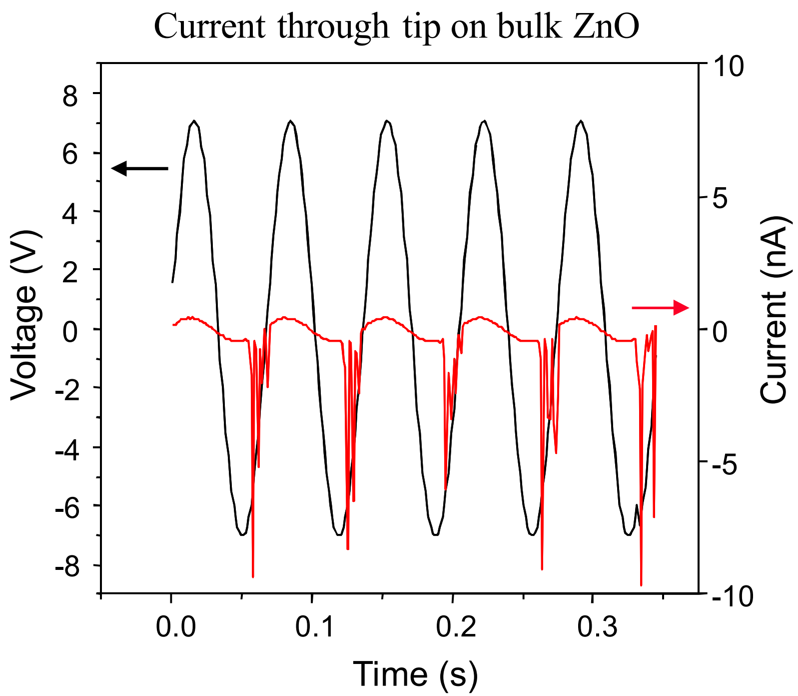




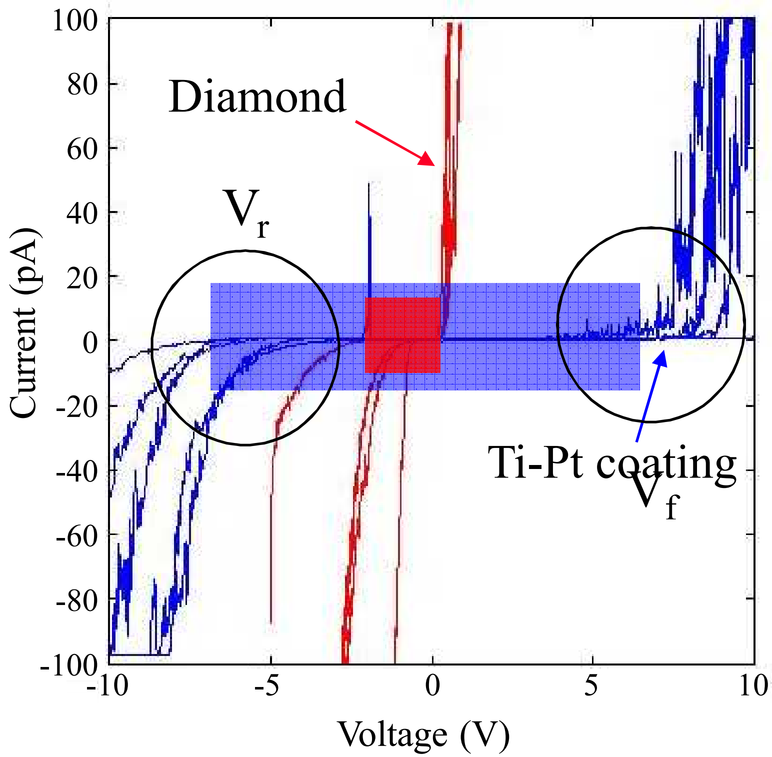
Similar work by:
Park *et al*. APL, 24, 4358 (2003).
Pan *et. al*. Nanotech., 16, 1069, (2005).

I-V Curves using C-AFM





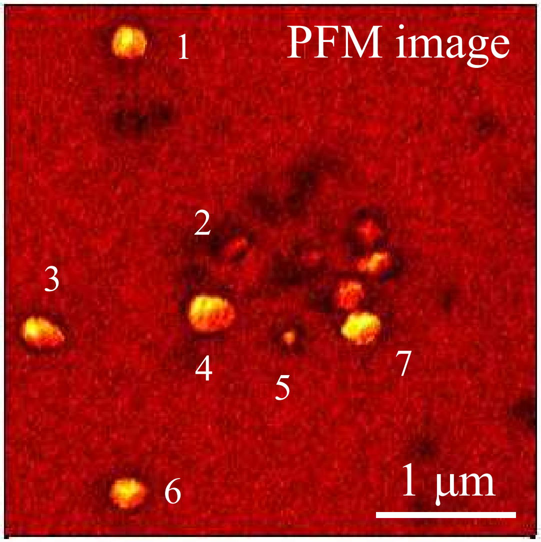
Current flow in nanorods

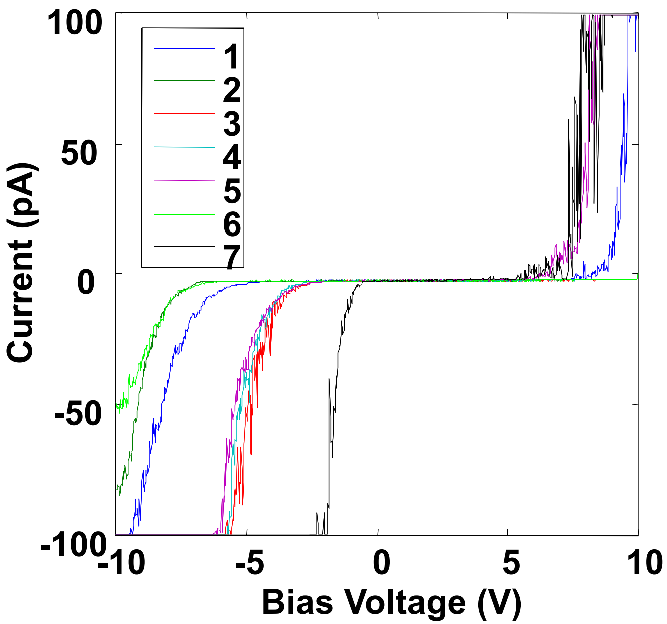


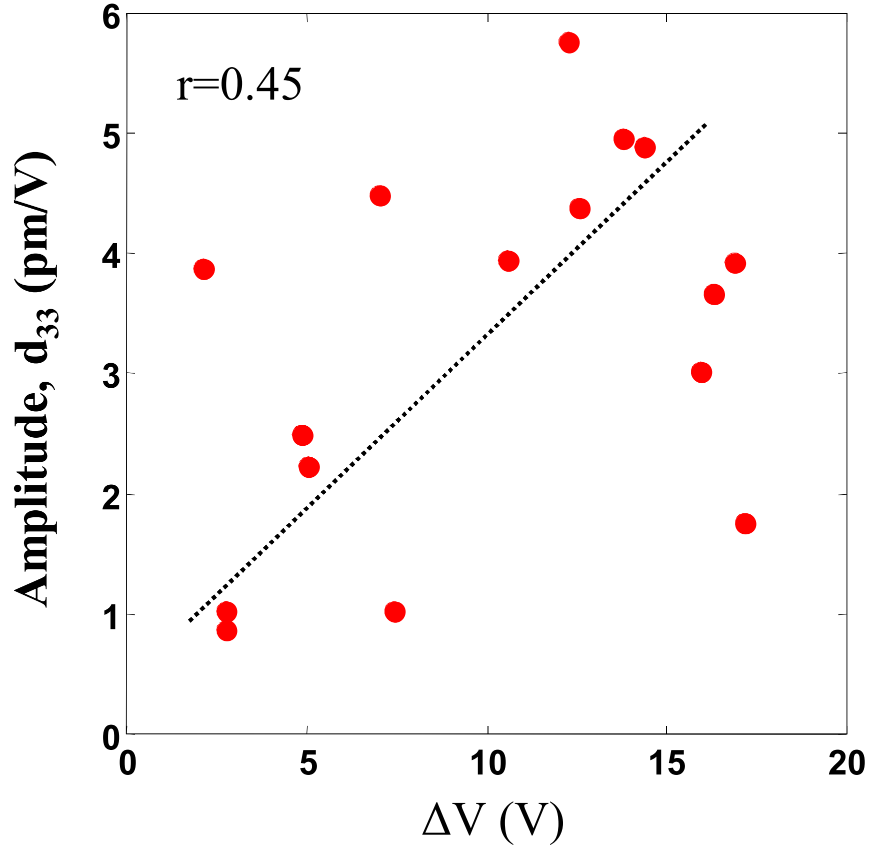
$\Delta V = (V_f - V_r)$

Higher ΔV = higher PFM?

I-V Curve Correlations







Conclusions/Future Work

- Nanorods grow [0001] oriented from Ag substrate
- Amplitude response is greater than single crystal ZnO
- Measured the I-V properties of individual nanorods
- Correlation between I-V properties and piezoelectric props

Future Work:

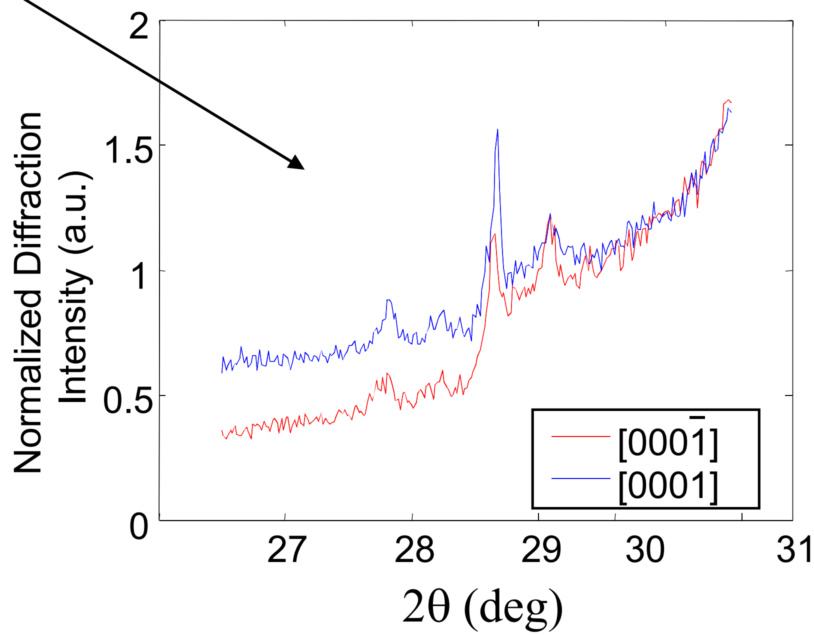
- Continue I-V studies
- High resolution current & PFM maps on individual nanorod
- Scanning Capacitance Microscopy

The End

Crystal polarity determination

Morphology
Etching
Piezoelectric Effect
Anomalous dispersion XRD
Scanning Probes
Coaxial impact ion spectroscopy
Convergent Beam TEM
Electron energy loss spectroscopy

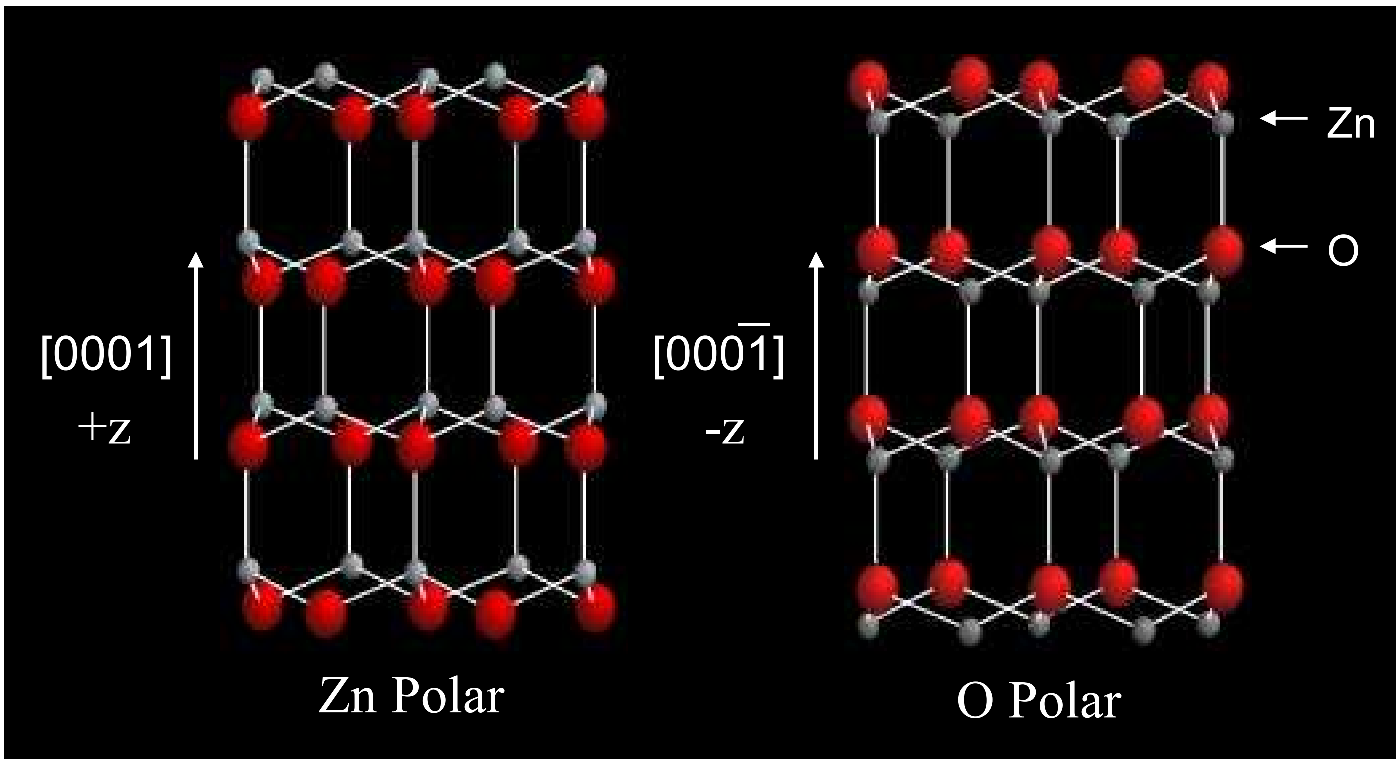
Characterize single crystal ZnO



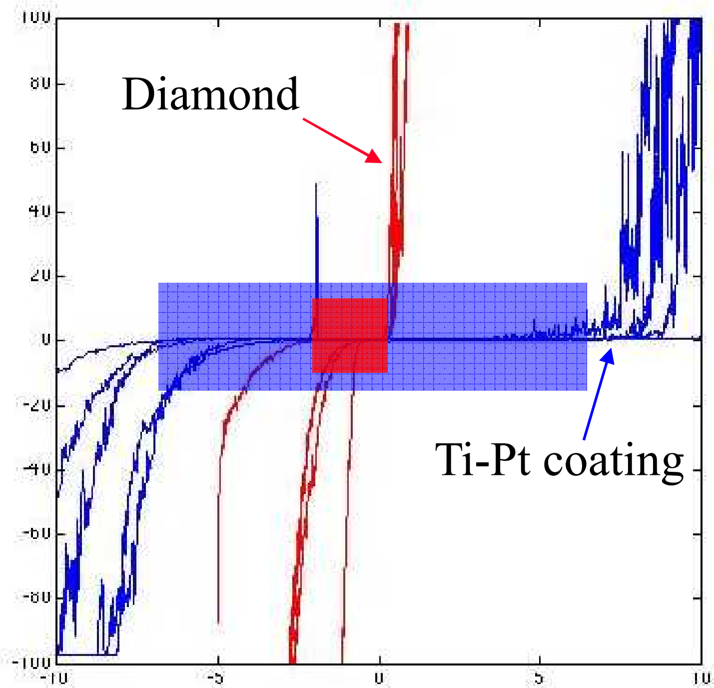
ZnO Crystal Structure

Crystal polarity ⟶ Defect incorporation, surface stability, piezoelectric, electric, optical properties

ZnO wurtzite structure $P6_3mc$ (6mm)



Tip Work function differences



ΔV

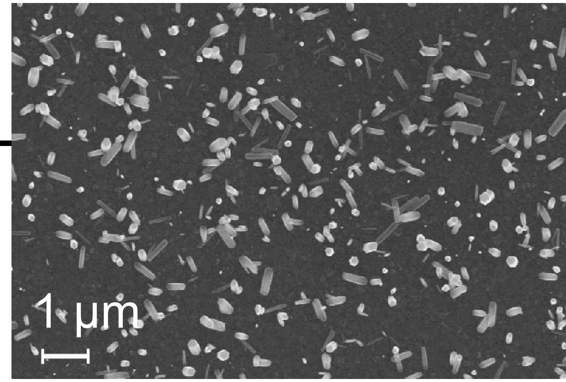
Larger voltages before current flow = higher PFM?

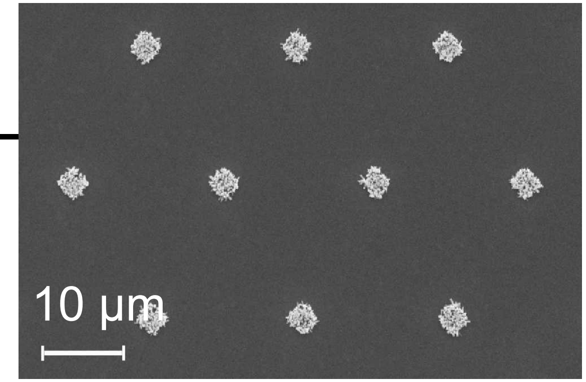
Side by side pfm & current maps

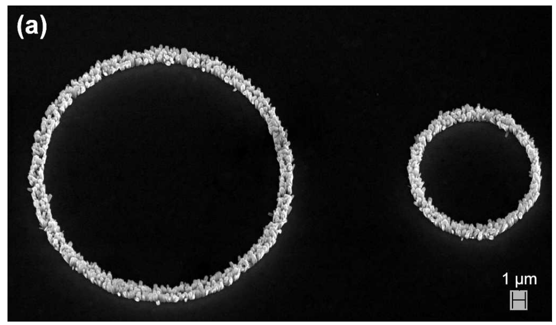
Carrier concentration is what we really want….

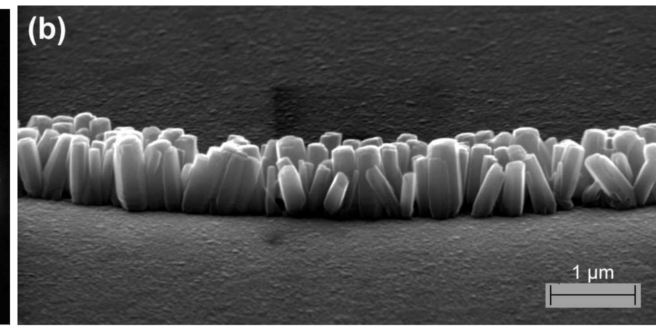
Fix Figure

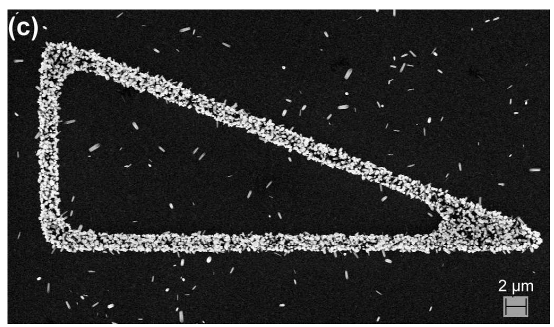
ZnO Nanorod Patterning

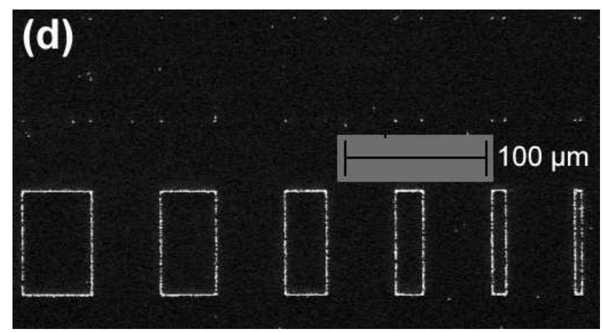


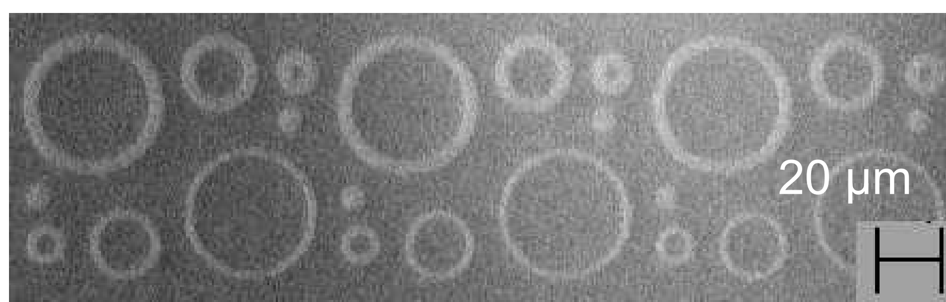








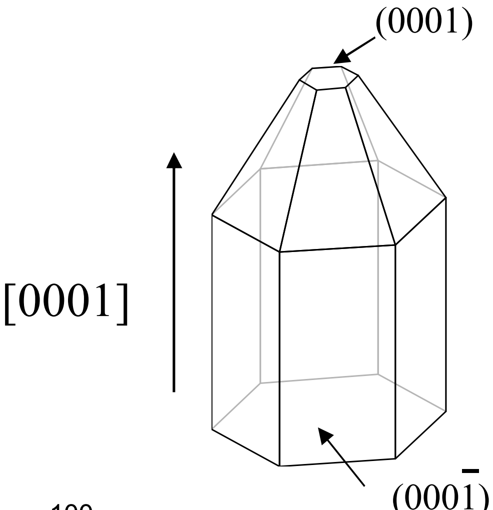


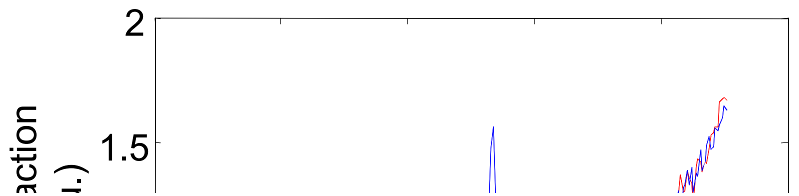


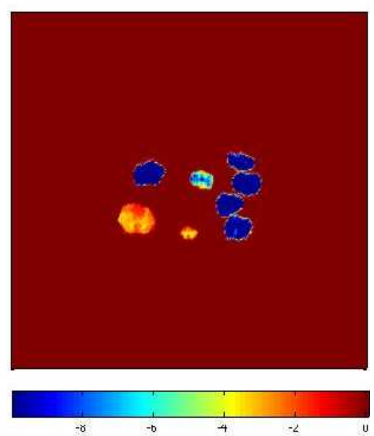
Sandia National Laboratories

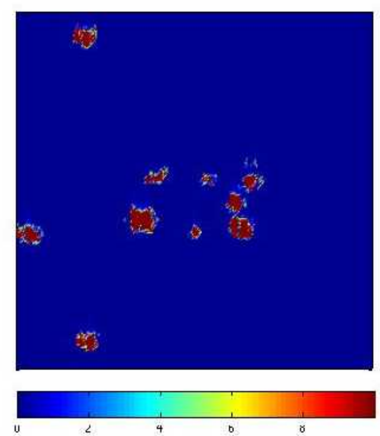
The piezoelectric effect is given as $\varepsilon_3 = d_{33}E_3$ where ε_3 is the strain, d_{33} is the piezoelectric coefficient, and E_3 is the applied field. In bulk ZnO, d_{33} is a *positive* value. This means:

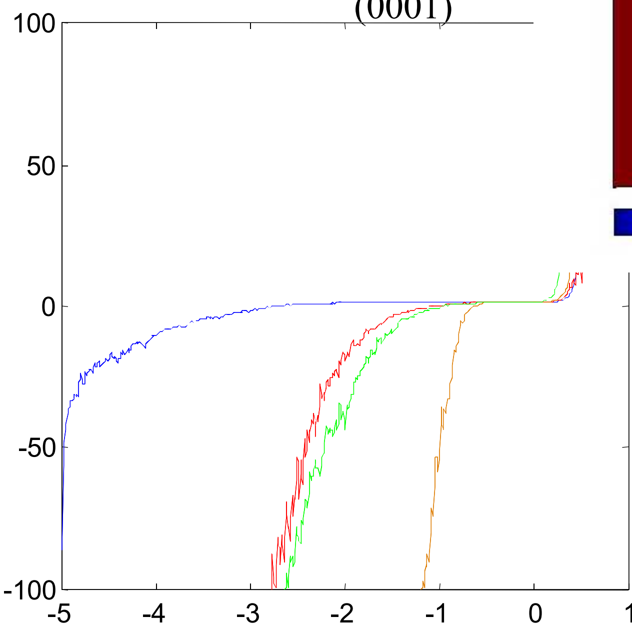
- +E applied parallel to [0001] = $(d_{33})(+E_3) = +\,\varepsilon_3$ *expansion*
- +E applied parallel to [000$\bar{1}$] = $(d_{33})(-E_3) = -\,\varepsilon_3$ *contraction*


(0001)
[0001]
(000$\bar{1}$)

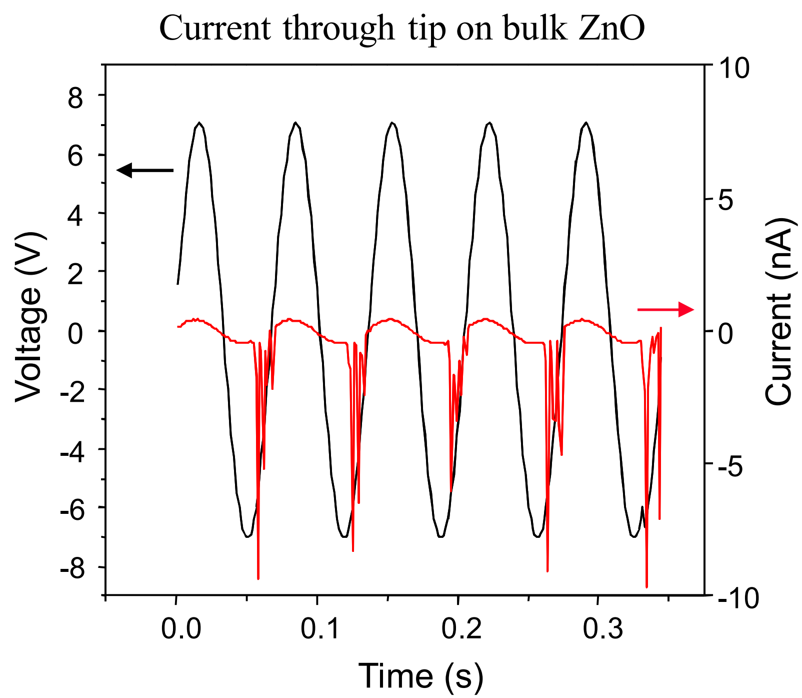

2
1.5






100
50
0
-50
-100
-5
-4
-3
-2
-1
0
1

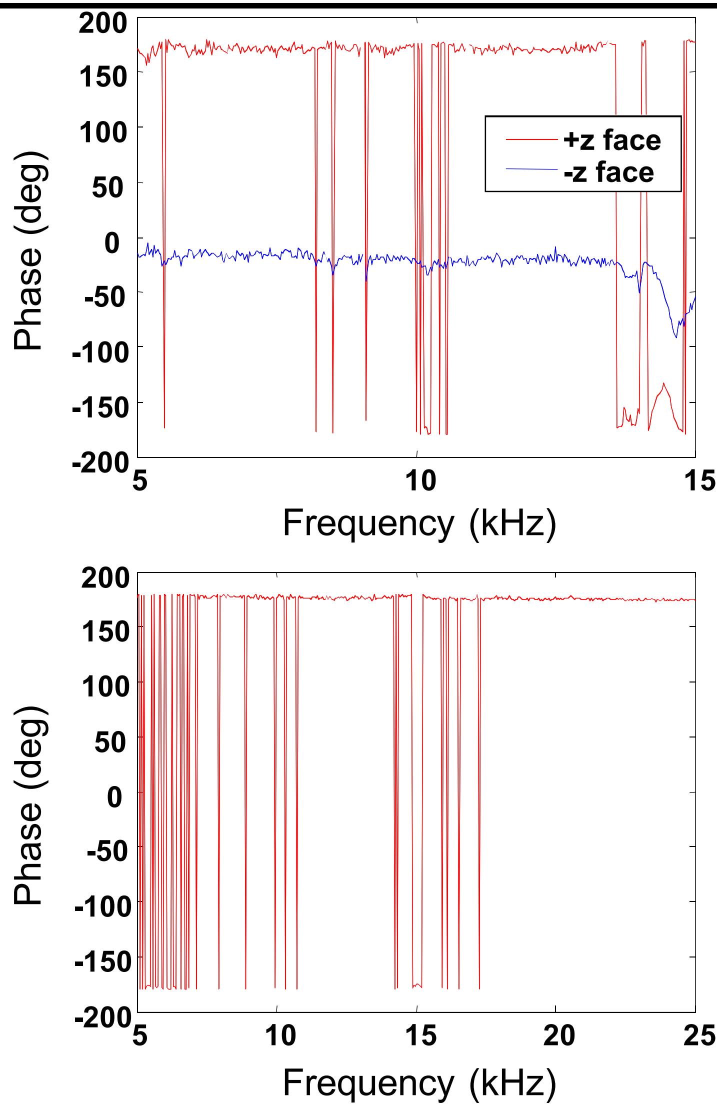
Current flow in nanorods



What are consequences of current flow on PFM measurements?

Ideally look at current & PFM simultaneously

ZnO Nanorod


200
150
100
50
0
-50
-100
-150
-200
Phase (deg)
5
10
15
Frequency (kHz)
+z face
-z face
200
150
100
50
0
-50
-100
-150
-200
Phase (deg)
5
10
15
20
25
Frequency (kHz)

Crystal polarity determination

Increasing difficulty

- Morphology
- Etching
- Piezoelectric Effect
- Anomalous dispersion XRD
- Scanning Probes
- Coaxial impact ion spectroscopy
- Convergent Beam TEM
- Electron energy loss spectroscopy

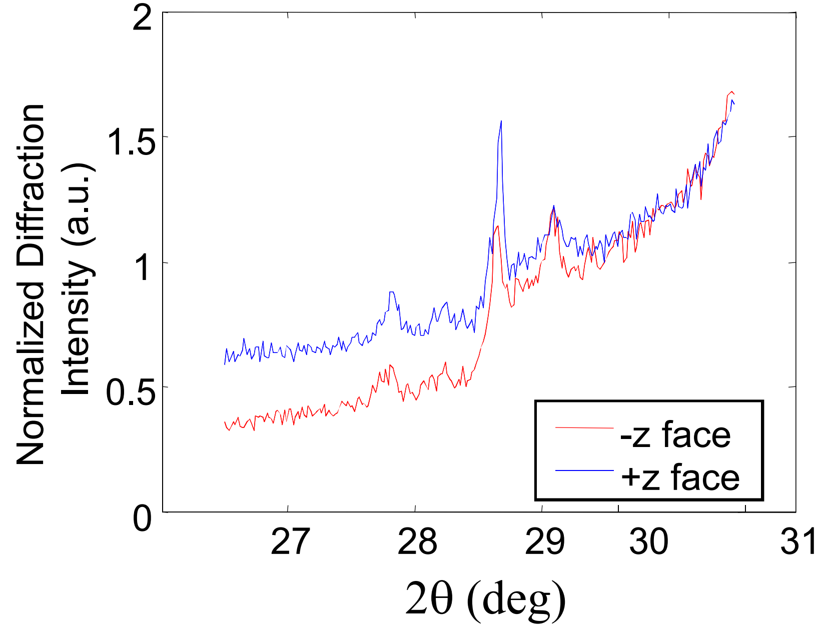
KCF Technologies www.kcftech.com/

Sandia National Laboratories

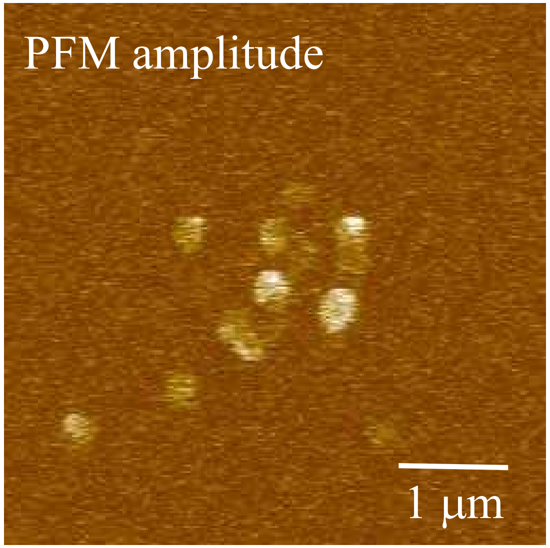
Crystal polarity determination

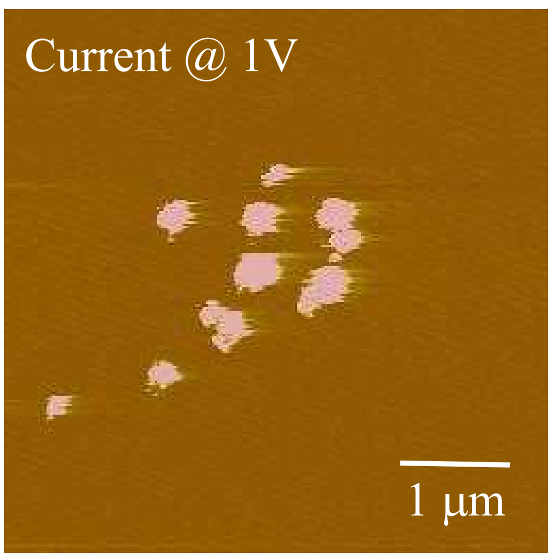
Increasing difficulty

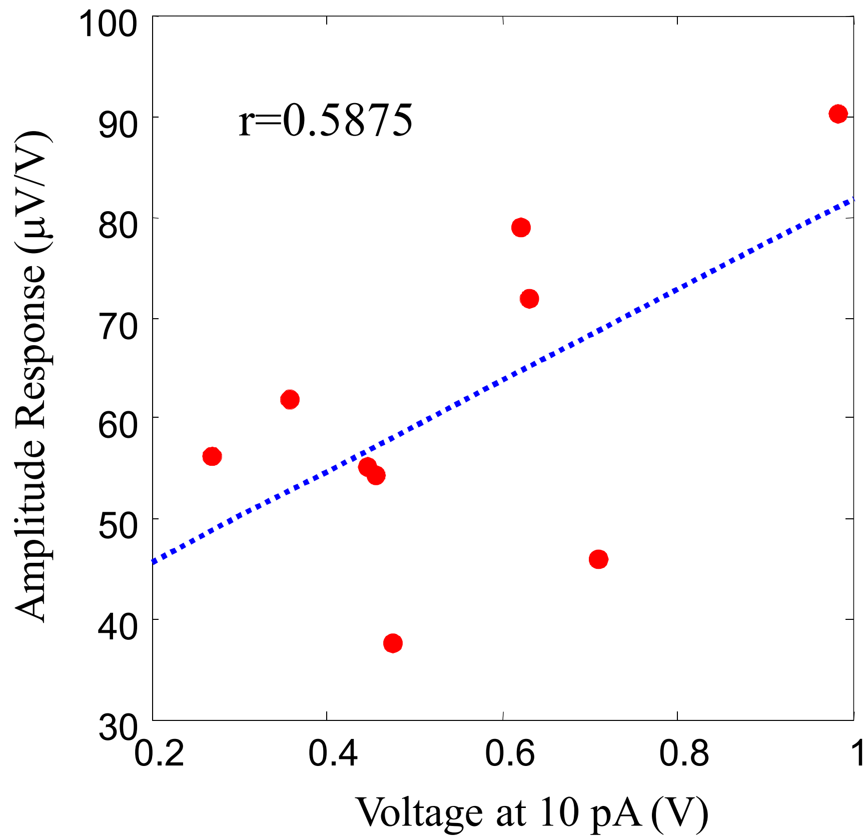
- Morphology
- Etching
- Piezoelectric Effect
- Anomalous dispersion XRD
- Scanning Probes
- Coaxial impact ion spectroscopy
- Convergent Beam TEM
- Electron energy loss spectroscopy



Correlations?



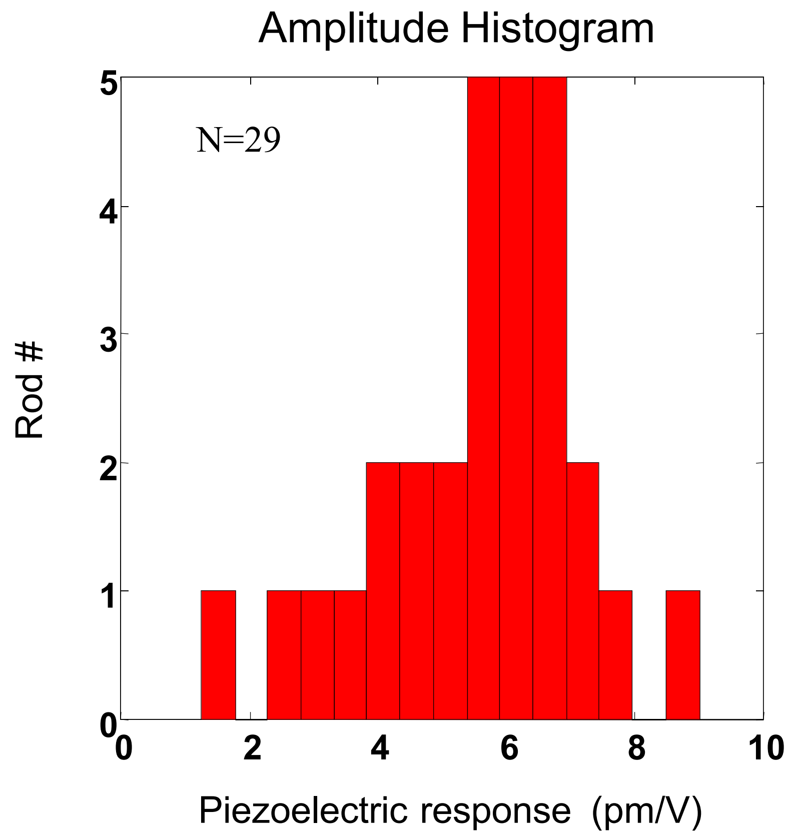


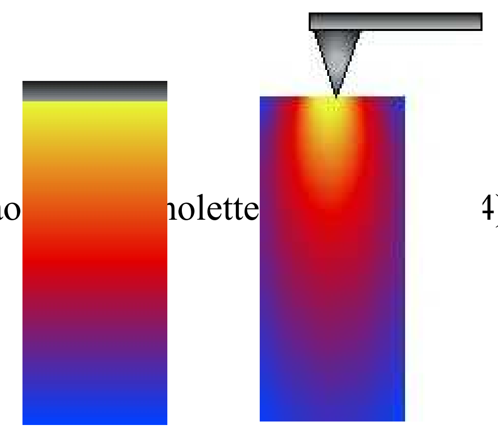


Piezoelectric Response (d_{33})

Amplitude Response

	Response (pm/V)	Ratio
Bare ZnO +z face	**2.97 ± 0.57**	
Nanorods	**5.61 ± 1.61**	**1.9**
$LiNbO_3$	**7.17 ± 0.76**	





Zhao nolette 4).

Piezoelectric Force Microscopy

- SFM Topographic Data (scan rate ~1-2 Hz)

+

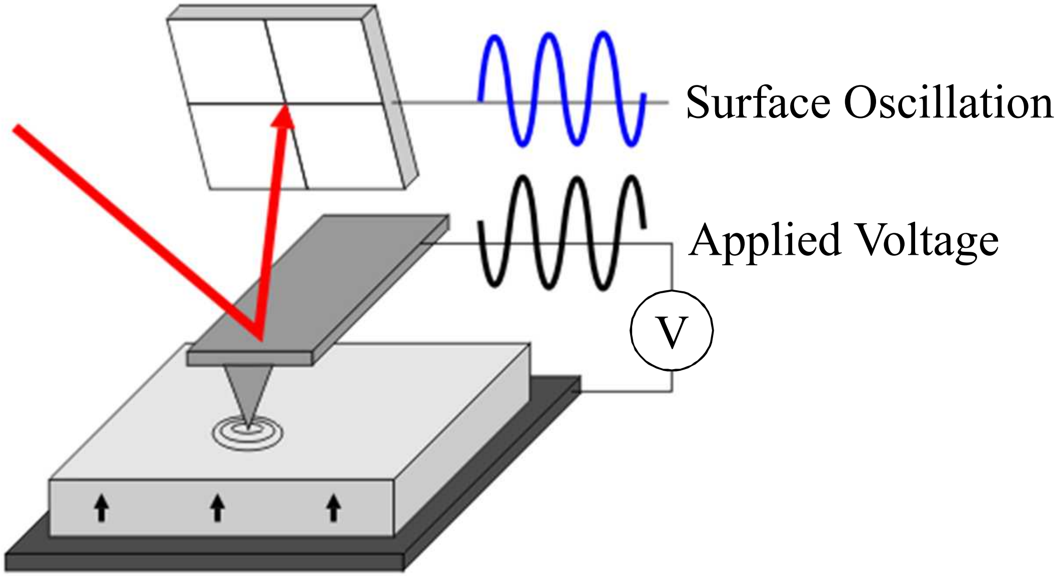
- Electromechanical Data (voltage ~ 1-25 kHz)

PFM Signal

$\varepsilon_3 = (d_{33})(E_3)$

$+\varepsilon_3 = (d_{33})(+E_3)$

$-\varepsilon_3 = (d_{33})(-E_3)$



Spatial variation :

- Amplitude
- Phase → $[000\bar{1}]$ face = **In phase** with AC voltage

[0001] face = **Out of phase** with AC voltage

Piezoelectric Force Microscopy

- SFM Topographic Data (scan rate ~1-2 Hz)

+

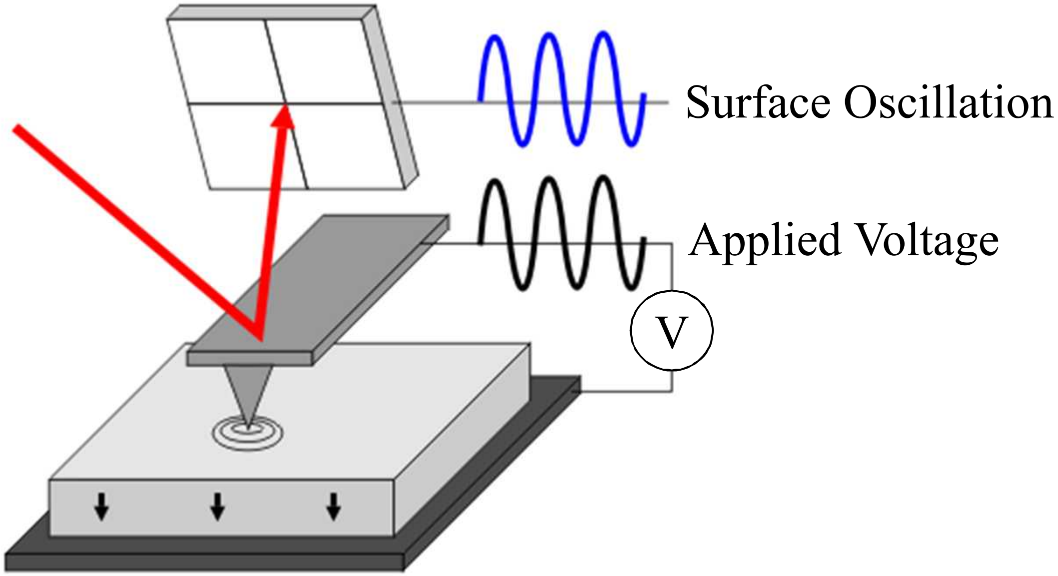
- Electromechanical Data (voltage ~ 1-25 kHz)

PFM Signal

$\varepsilon_3 = (d_{33})(E_3)$

$+\varepsilon_3 = (d_{33})(+E_3)$

$-\varepsilon_3 = (d_{33})(-E_3)$



Spatial variation :

- Amplitude
- Phase → $[000\bar{1}]$ face = **In phase** with AC voltage

I-V Curves using C-AFM