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Coupled Piezoelectric and Electrical Properties of Individual ZnO Nanorods

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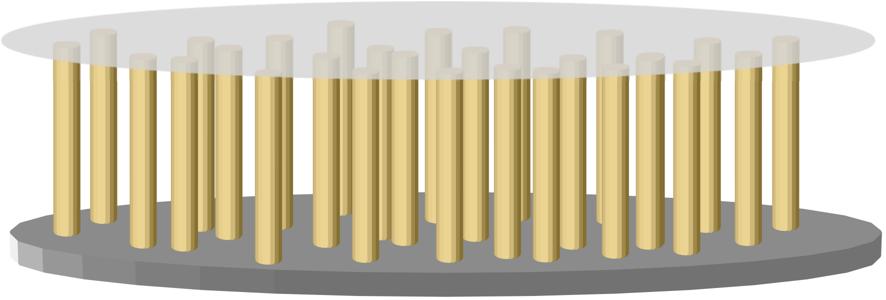
Session A: ZnO Nanostructures
EMC Meeting, June 25, 2007

Sandia Truman Fellowship

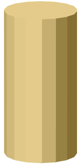
Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company,
for the United States Department of Energy's National Nuclear Security Administration
under contract DE-AC04-94AL85000.

Motivation of this work is to examine the properties of individual nanostructured ZnO

Ensemble measurements

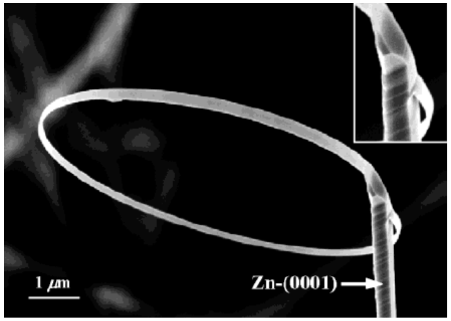


Individual measurements

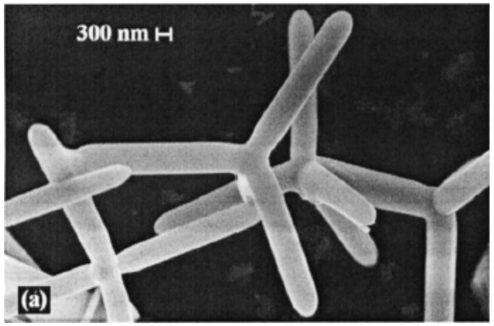


Zinc oxide is a key nanomaterial due to ease of synthesis and interesting properties

Thermal Evaporation

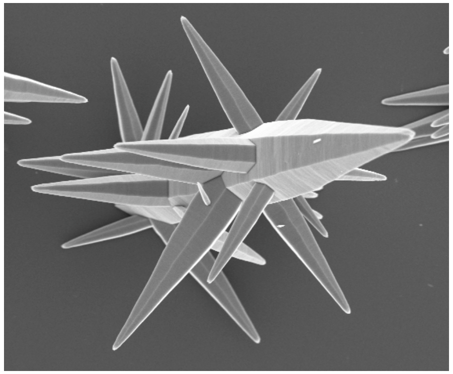


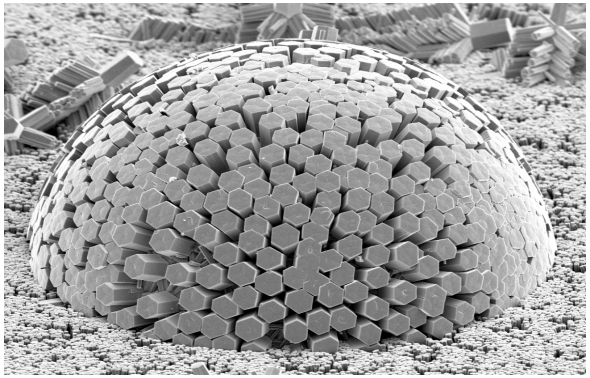
JAP, 97, 044304 (2005)

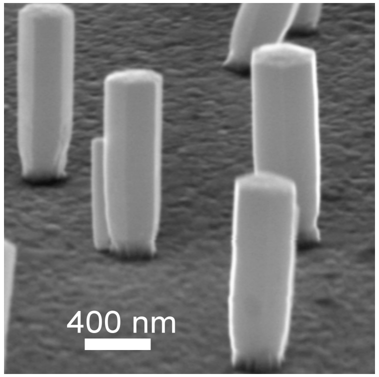


APL, 84, 2635 (2004)

Aqueous Solution Growth

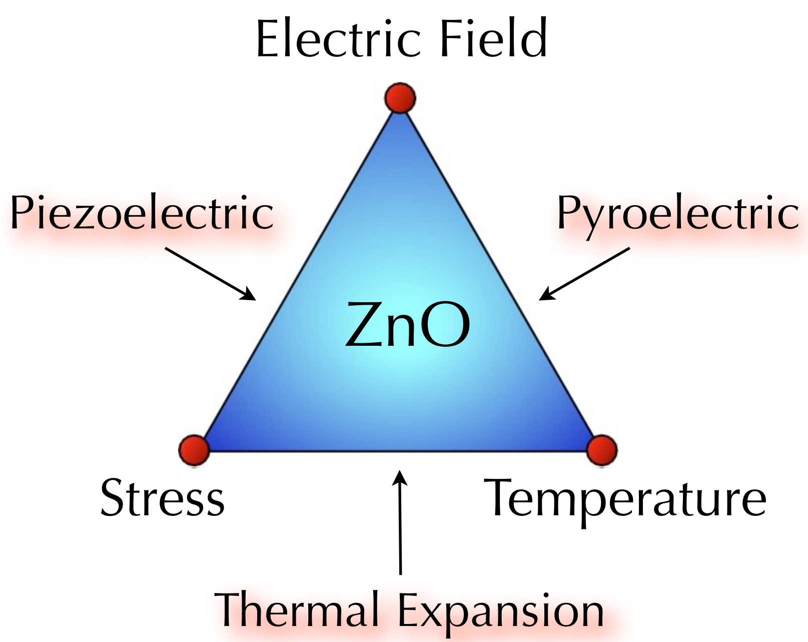






Zinc oxide is a key nanomaterial due to ease of synthesis and interesting properties

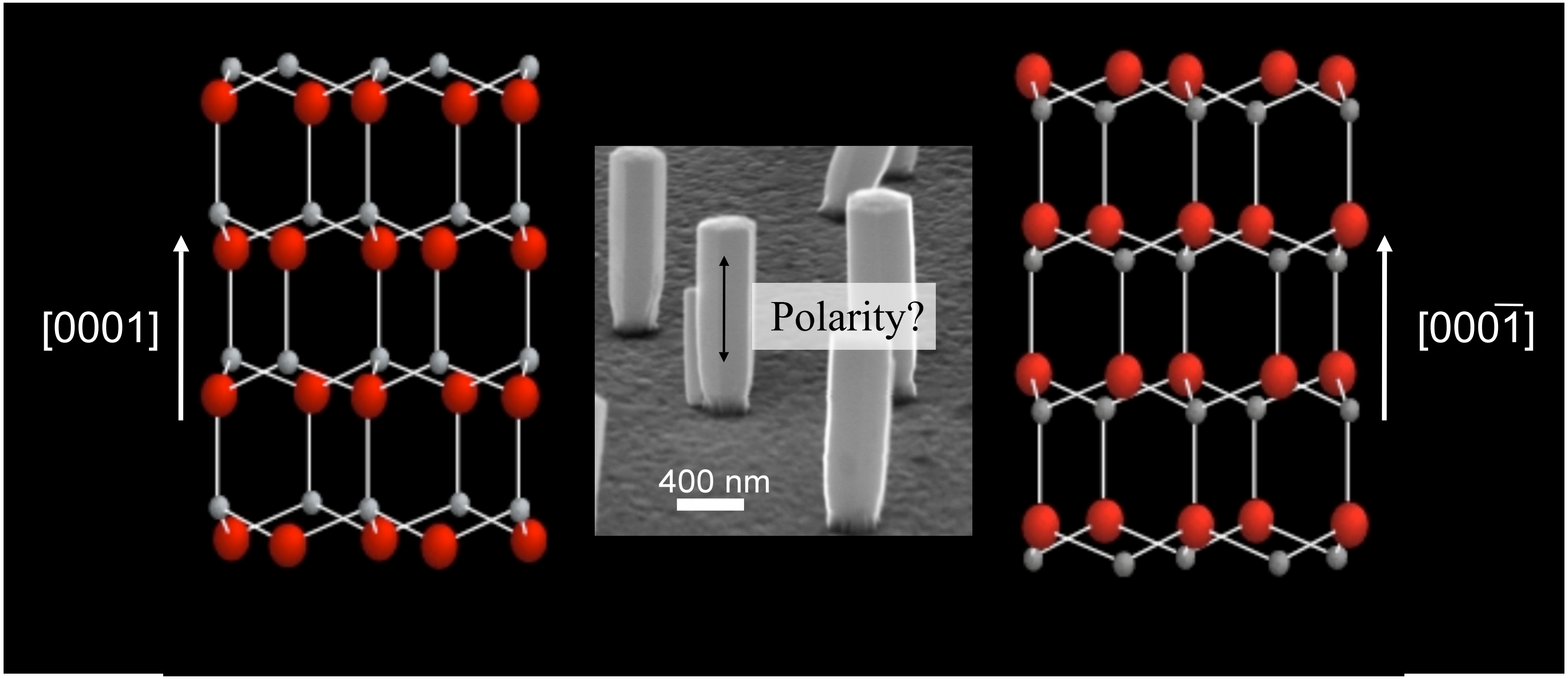
Semiconductor



ZnO crystal structure has permanent dipole which gives rise to piezoelectric effect

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

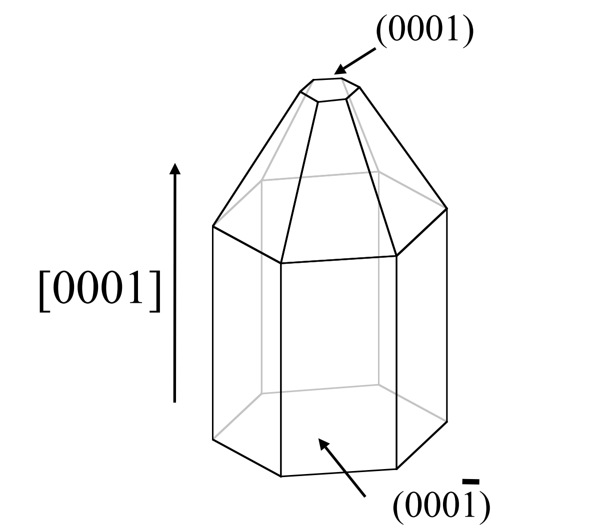
ZnO wurtzite structure P6_3mc (6mm)



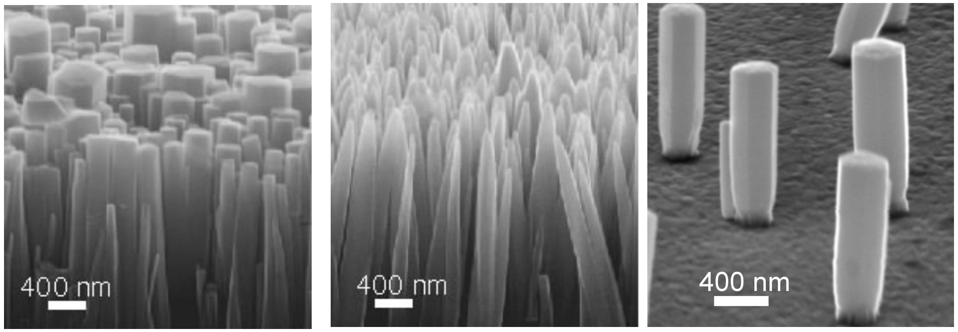
Crystal polarity is determined using piezoelectric force microscopy

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).



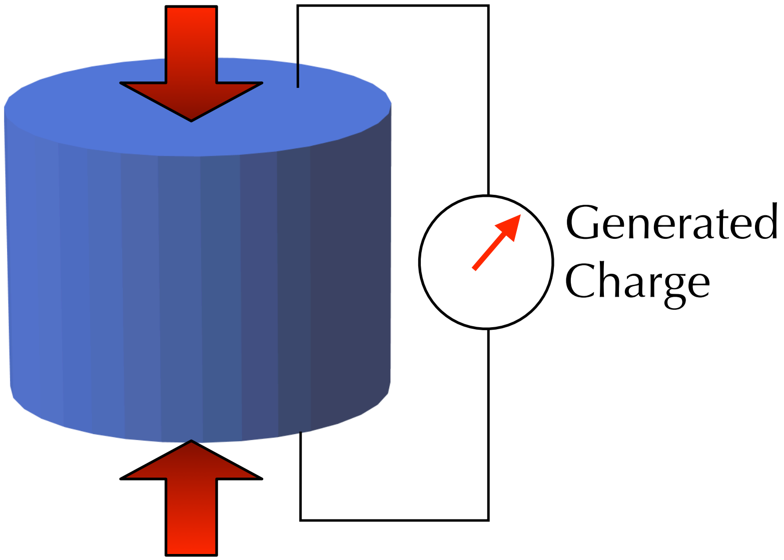
Crystal polarity is determined using piezoelectric force microscopy

Increasing difficulty

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

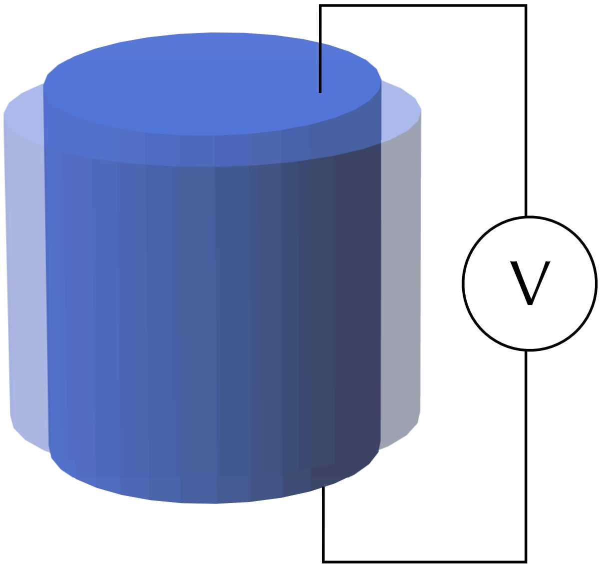
Piezoelectric effect relates the mechanical state to the electrical state in a material

Direct Effect



Stress → Charge

Converse Effect



Voltage → Deformation

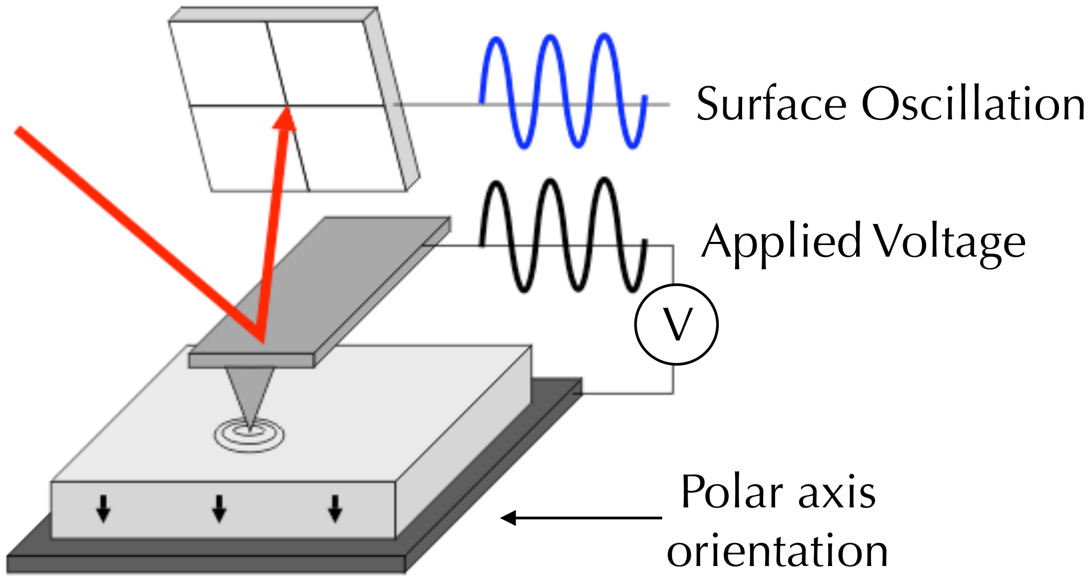
$$\varepsilon_3 = d_{33} E_3$$

Piezoelectric force microscopy (PFM) is used to measure nanoscale piezoelectric response

Topographic Data

+

Piezoelectric Data



Spatial variation :

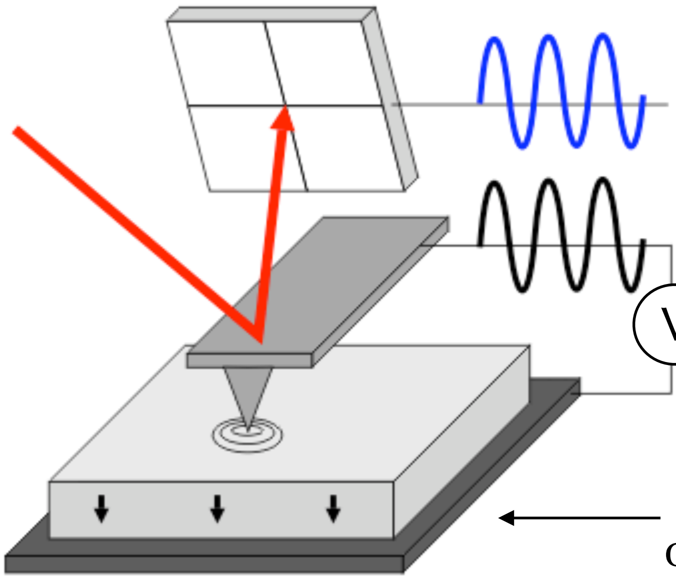
- Amplitude → Strength of piezoelectric response (d_{33})
- Phase

Piezoelectric force microscopy (PFM) is used to measure nanoscale piezoelectric response

Topographic Data

+

Piezoelectric Data



Spatial variation :

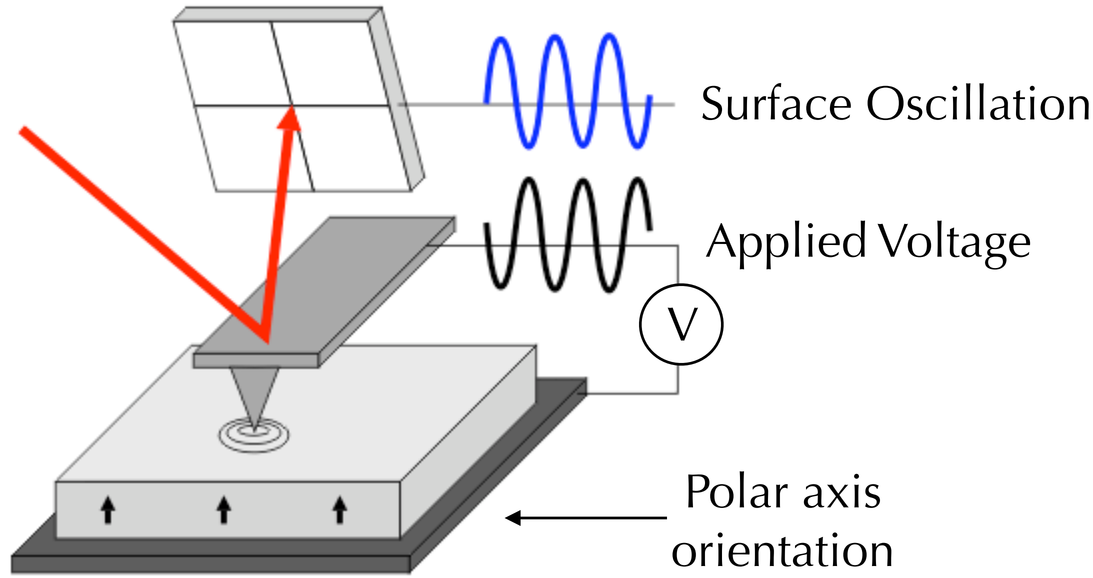
- Amplitude
- Phase ⟶ [0001] face = **In phase** with AC voltage

Piezoelectric force microscopy (PFM) is used to measure nanoscale piezoelectric response

Topographic Data

\+

Piezoelectric Data

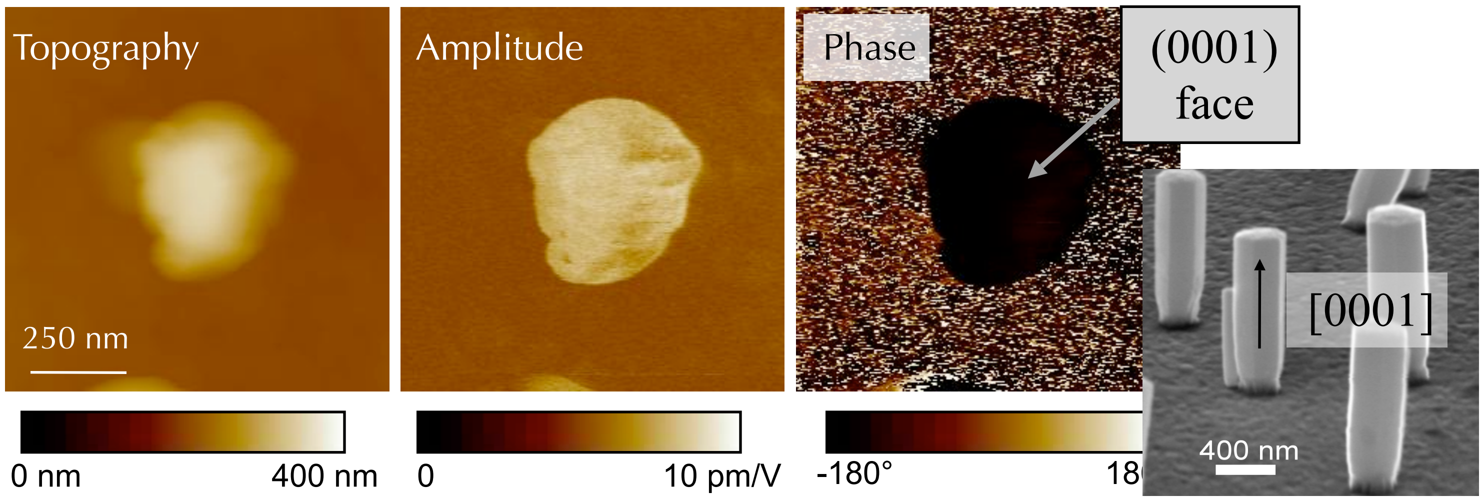


Spatial variation :

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

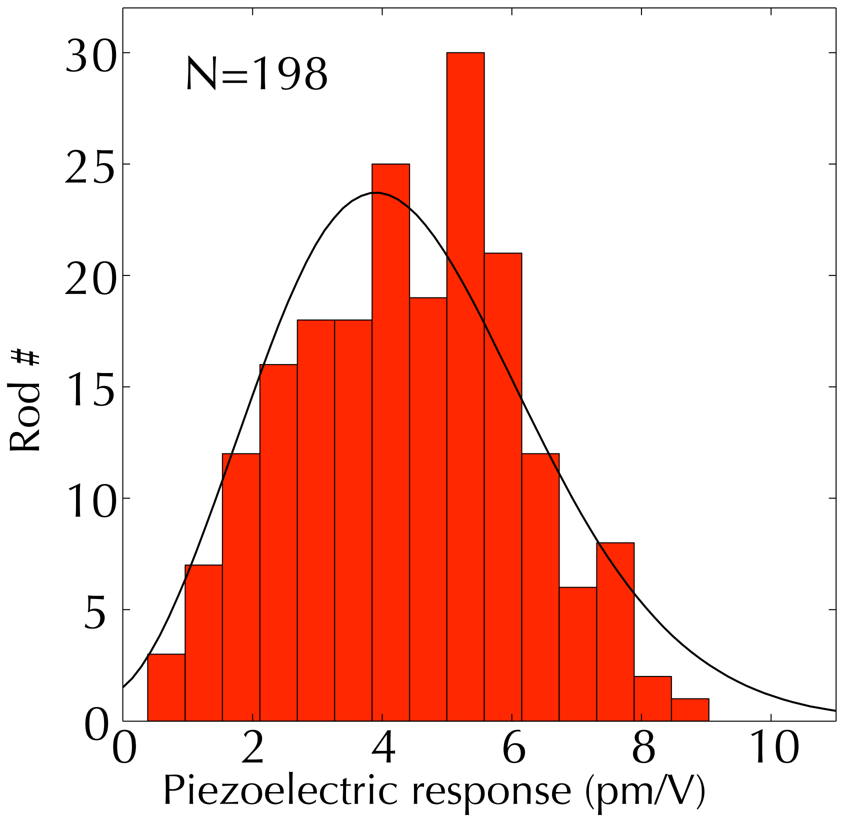
$[0001]$ face = **Out of phase** with AC voltage

PFM measures strength of d_{33} response and determines crystal orientation



D. A. Scrymgeour, *et al*, JAP, 101, 014316; (2007).

Piezoelectric response of ZnO nanorods shows a distribution of magnitudes



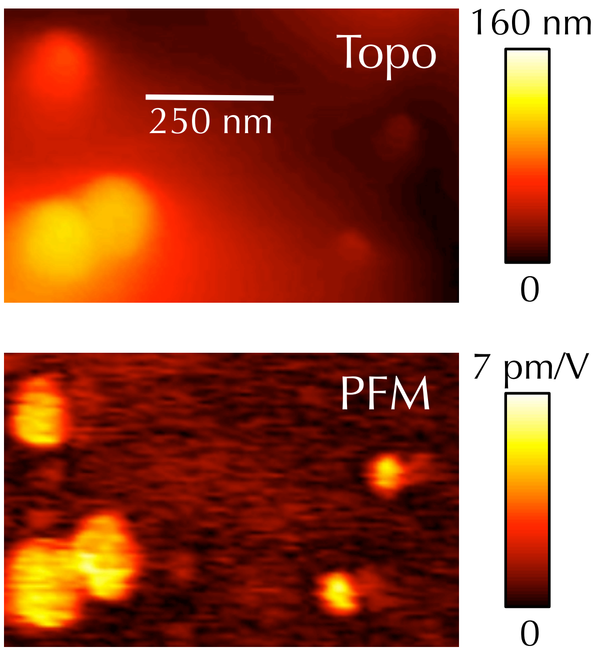
Nanorods 4.41 ± 1.73 pm/V

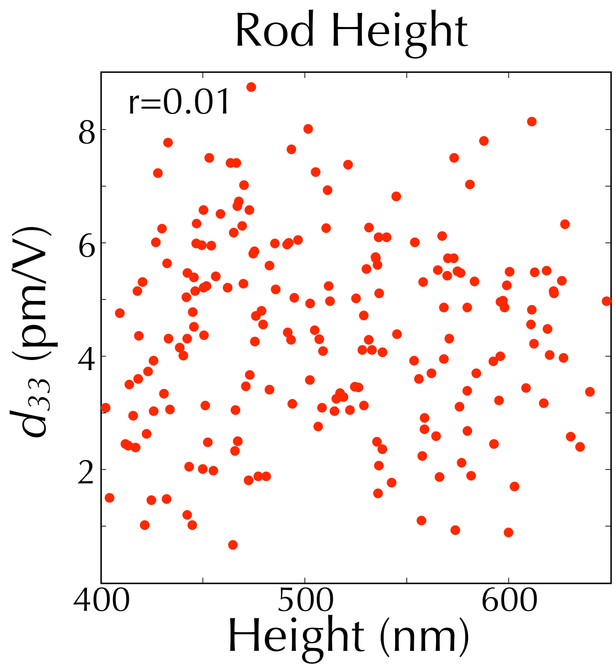
0.67 to 8.87 pm/V

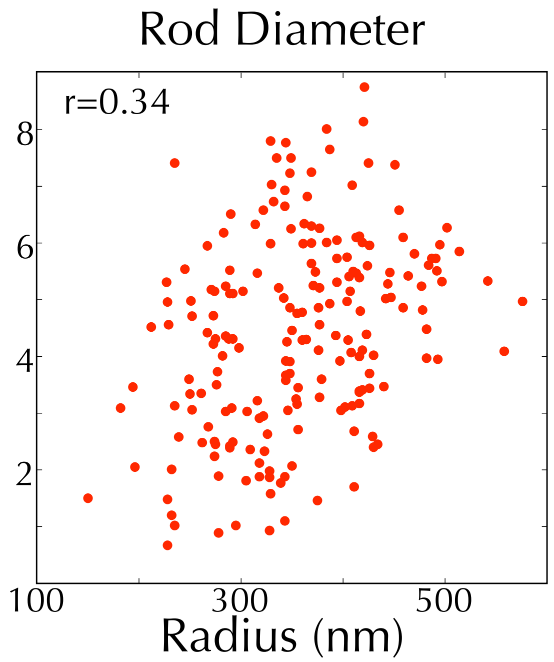
Li-doped ZnO 12.4 pm/V

D.A.Scrymgeour et al, JAP, 101, 014316 (2007).

Piezoelectric variation is not correlated to physical dimensions of nanorods



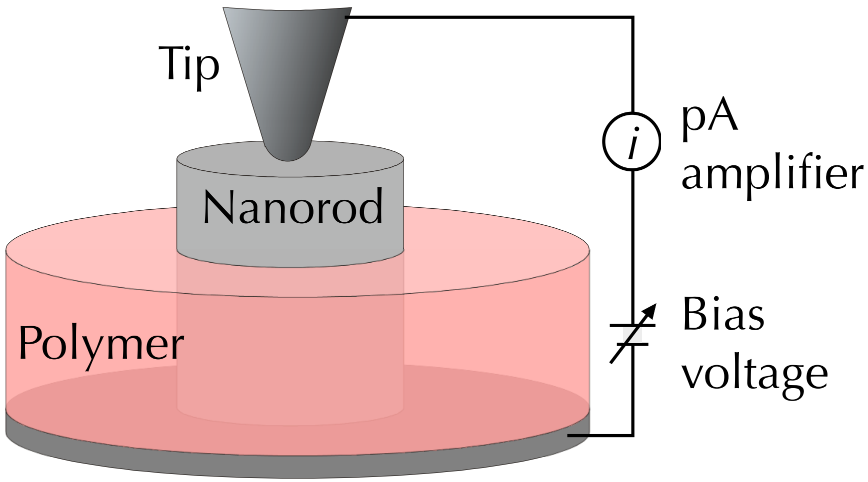


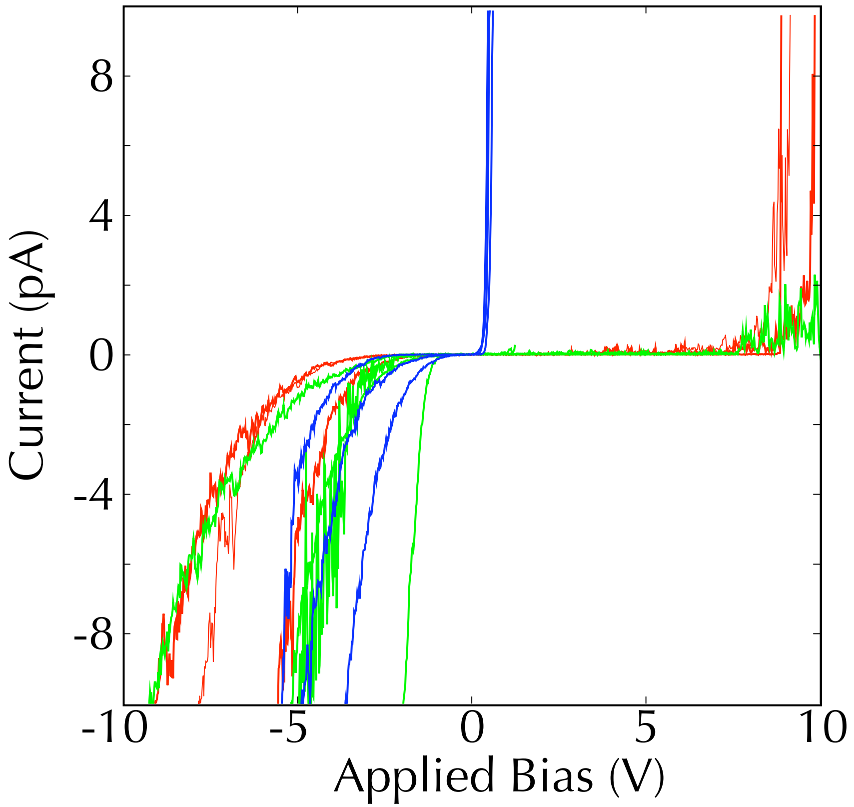


Suspect electrical properties

Conductive AFM is used to determine intrinsic electrical properties of nanorods

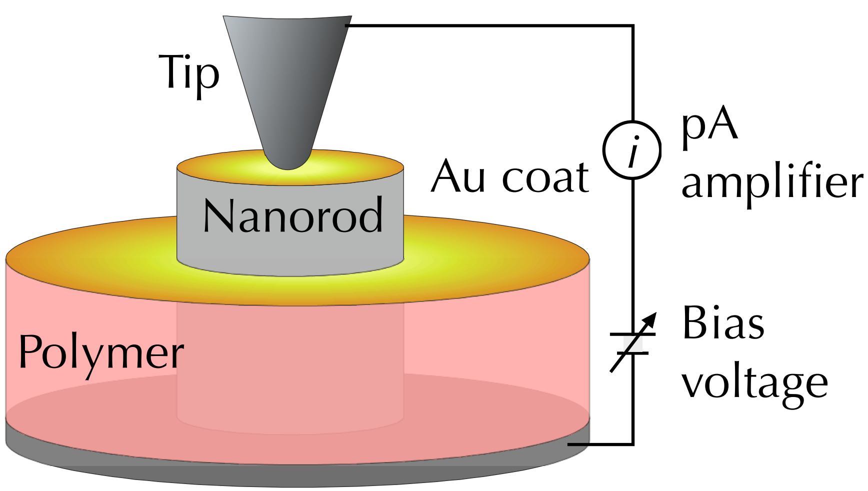
Ordinarily non-ohmic contacts with AFM tip

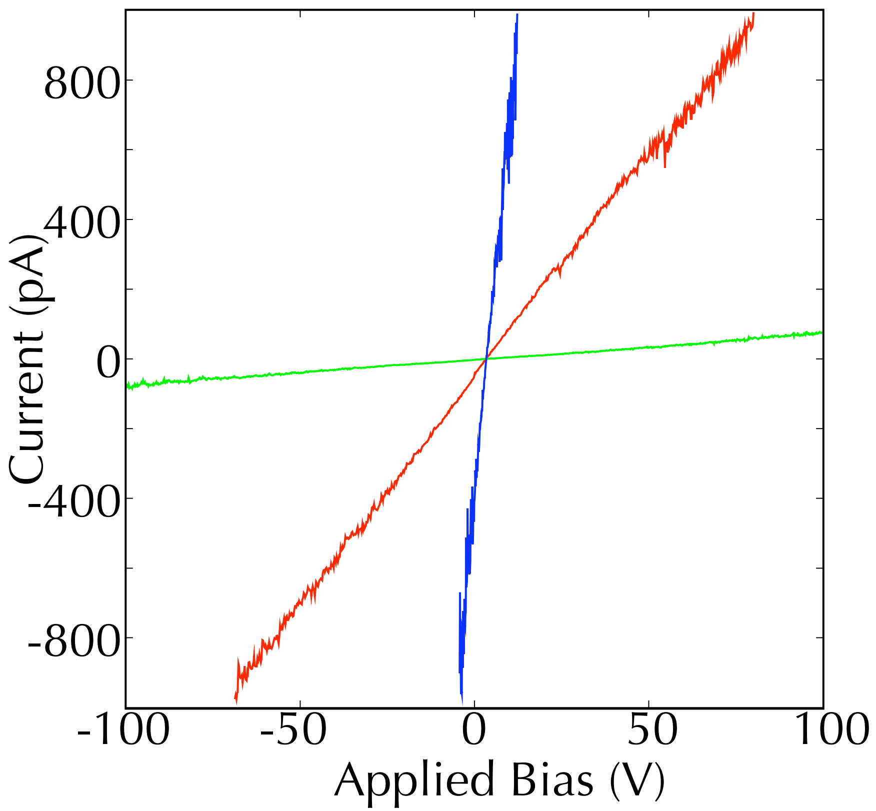




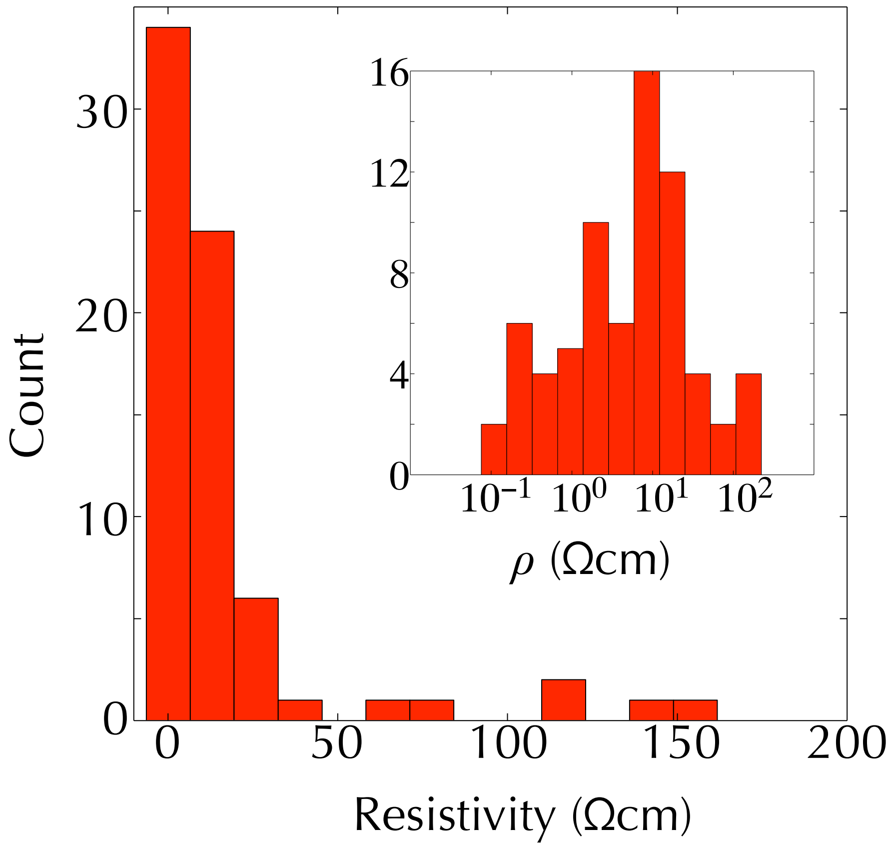
Conductive AFM is used to determine intrinsic electrical properties of nanorods

Annealed and coated rods form ohmic contacts with AFM tip





There is a large variation of resistivity in single population of ZnO nanorods



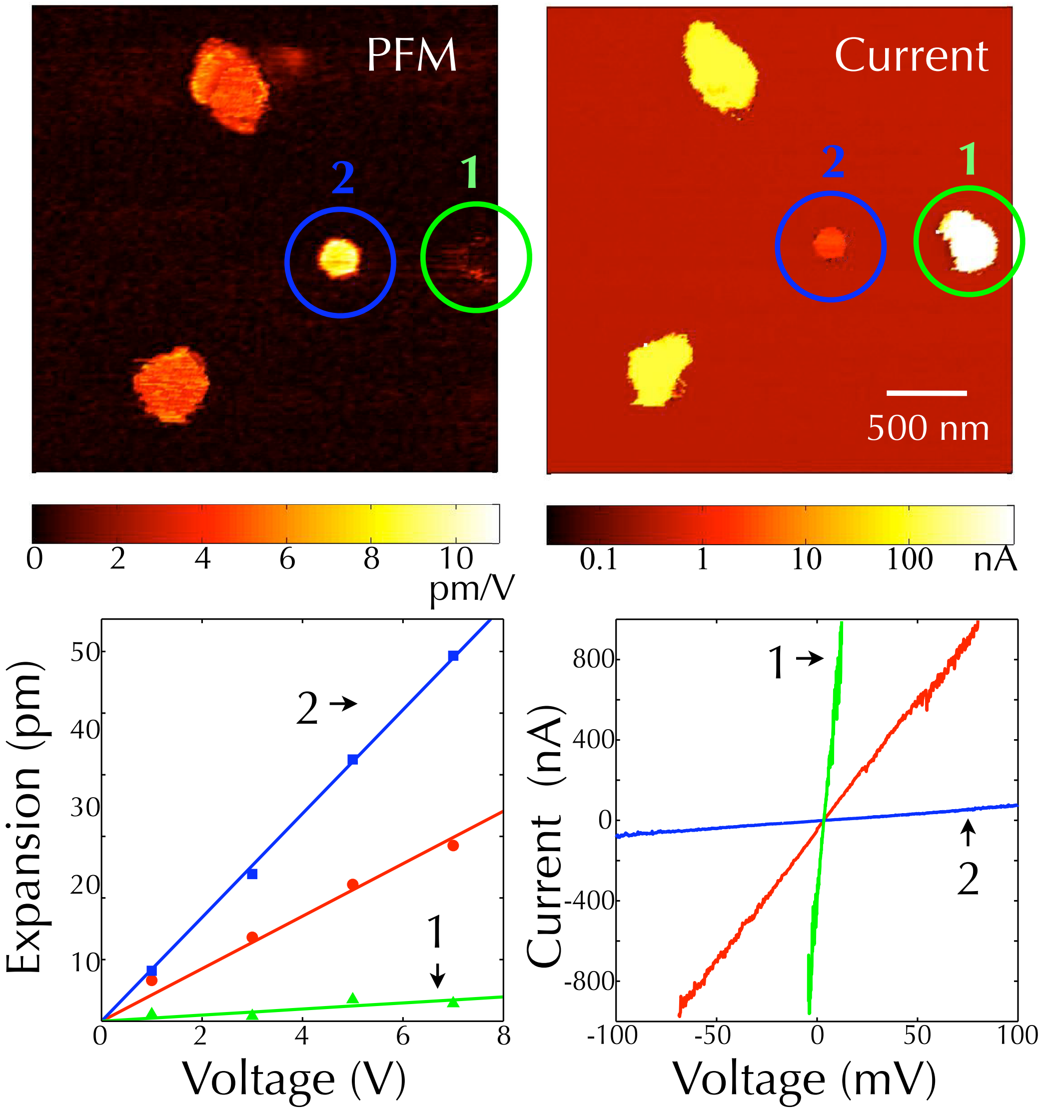
$$\rho = \frac{RA}{L}$$

Resistivity 0.1 - 155 Ωcm

Carrier concentration ~10^{16}-10^{19} cm^{-3}

Not related to physical dimensions

Piezoelectric response and resistance are correlated in individual rods



Low d_{33} ↔ High current

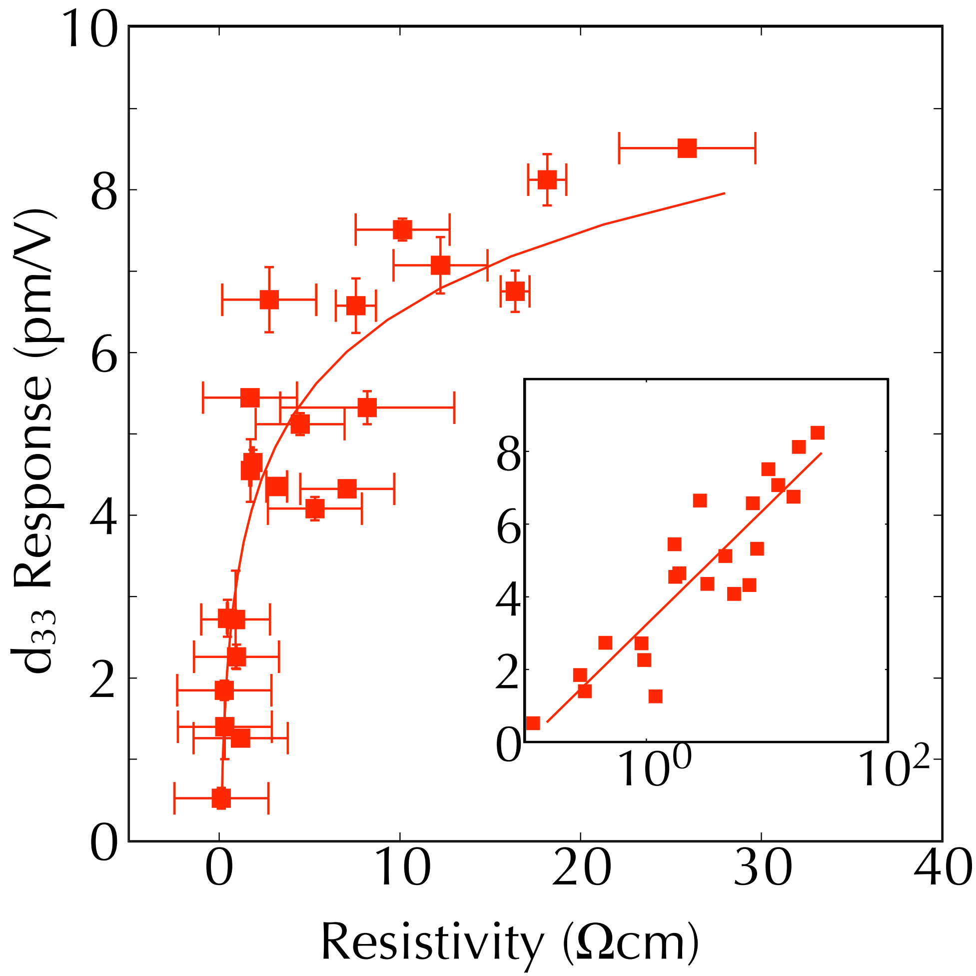
High d_{33} ↔ Low current

0.5 pm/V → 15 kΩ

4.3 pm/V → 79 kΩ

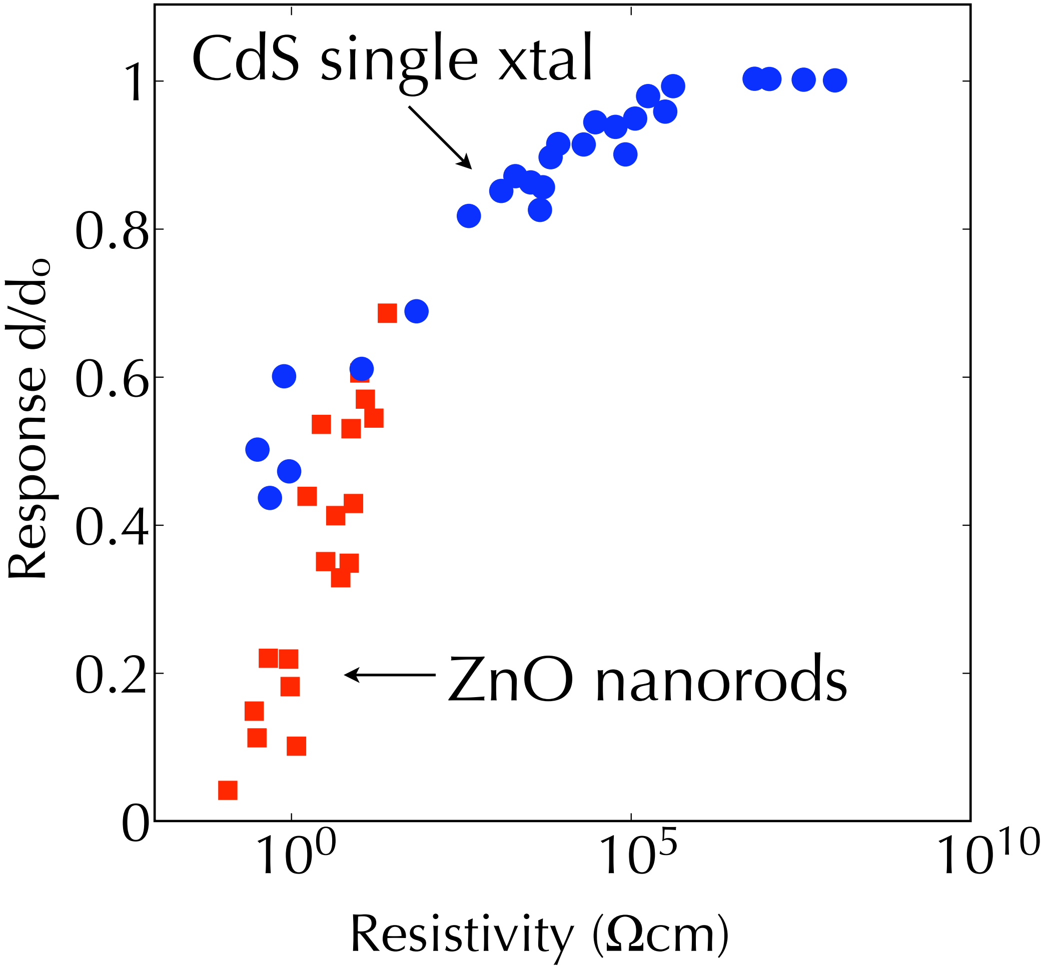
8.4 pm/V → 1.3 MΩ

Piezoelectric response correlates directly with the resistivity of nanorods



D. A. Scrymgeour, *et al*, Nano Letters , *in press*, (2008).

ZnO nanorod response similar to other piezoelectric semiconductors

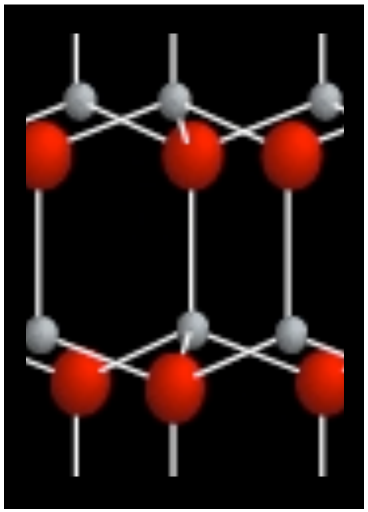


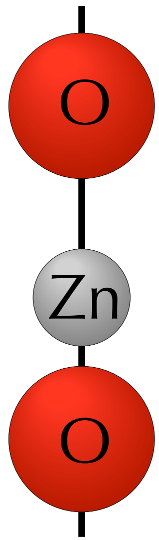
Ohmic contacts prevent electric shielding.

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

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

Bond strength along polar axis is related to the strength of the piezoelectric effect





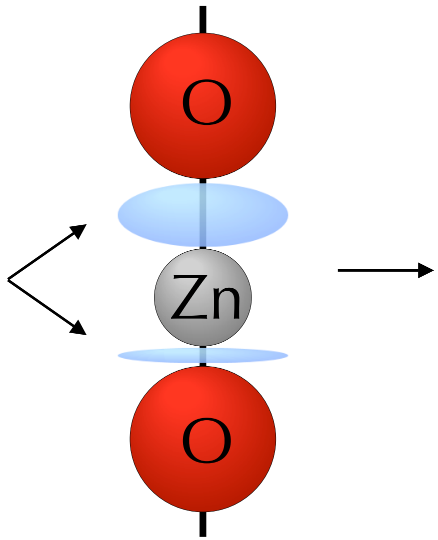
The Madelung energy is the bond strength in an ionic crystal

$$\alpha_M = 2(1 - \tfrac{1}{2} + \tfrac{1}{3} - \cdots)$$
$$= 2\ln(2)$$

Electrostatic attraction in crystal

Shielding of ionic bonds by conduction electrons reduces piezoelectric response

Conduction electrons



The Madelung energy is the bond strength in an ionic crystal

$$\alpha_M = e^{-k_s R_o} - \tfrac{1}{2} e^{-2k_s R_o} + \tfrac{1}{3} e^{-3k_s R_o} - \cdots$$
$$= 2\ln[1 + e^{-k_s R_o}]$$

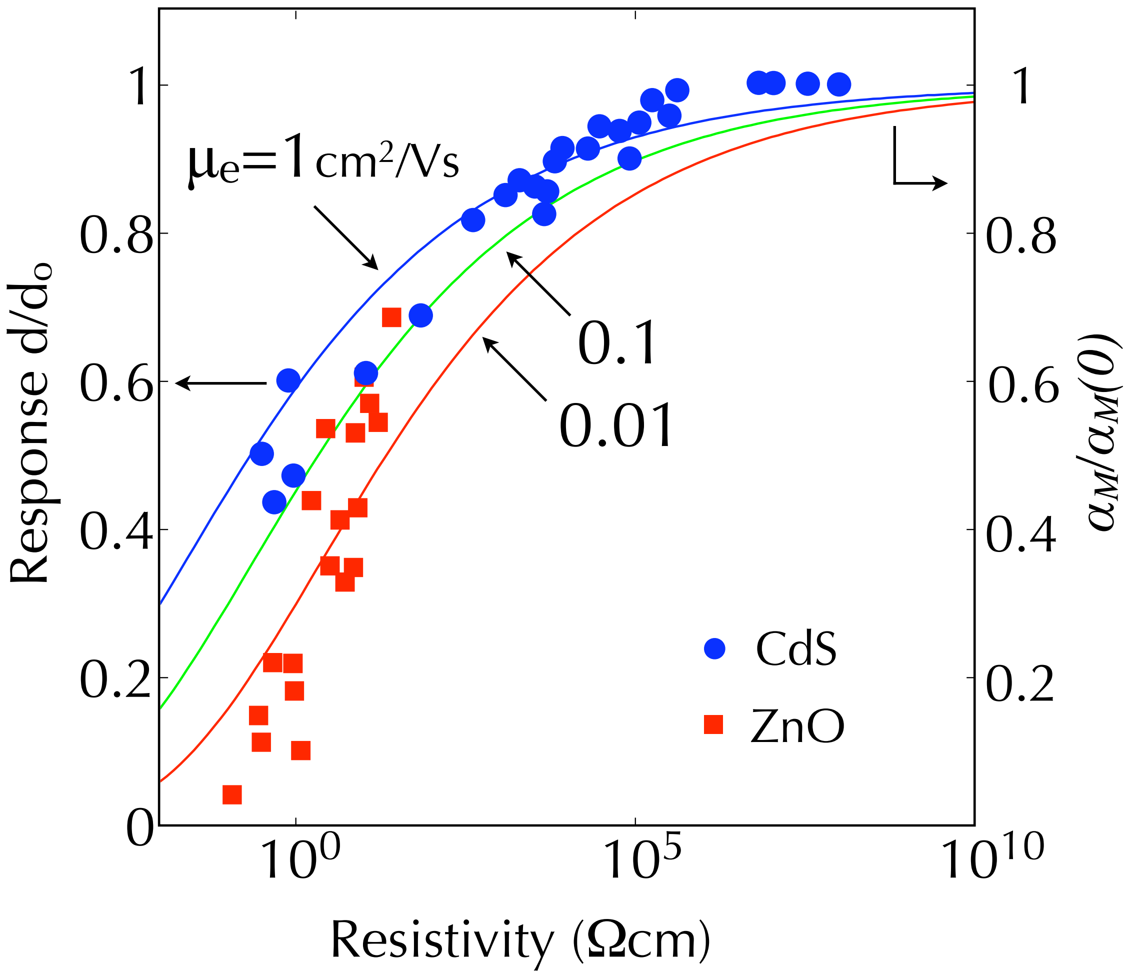
$$k_s = \sqrt{2}\left(\frac{3}{\pi}\right)^{1/6} \frac{\boxed{n_c^{1/6}}}{a_H^{1/2}}$$

Ratio of bond strength with electrons to that without

$$\frac{\alpha_M(n_c)}{\alpha_M(0)} < 1$$

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

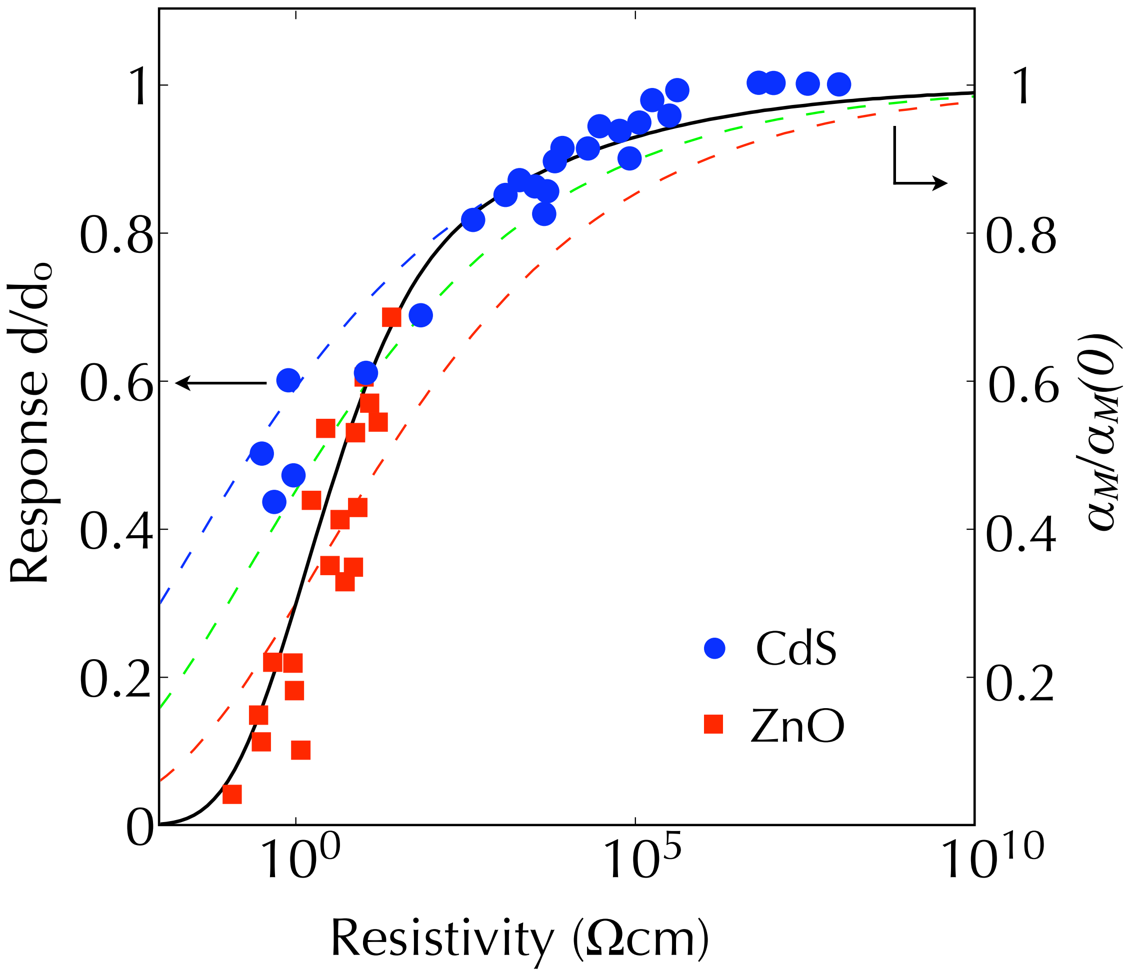
Madelung constant calculation with constant mobility does not model experimental data well



$$n_c = 1/\rho e \mu_e$$

Assumption that mobility, μ_e, constant as ρ changes

Madelung constant calculation with resistivity dependent mobility models data well



Mobility ↓ as:

- Scattering centers ↑
- Defects ↑

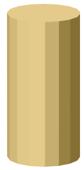
Mobility as a function of resistivity

$$\mu = \mu_o \frac{\rho}{\rho_o + \rho}$$

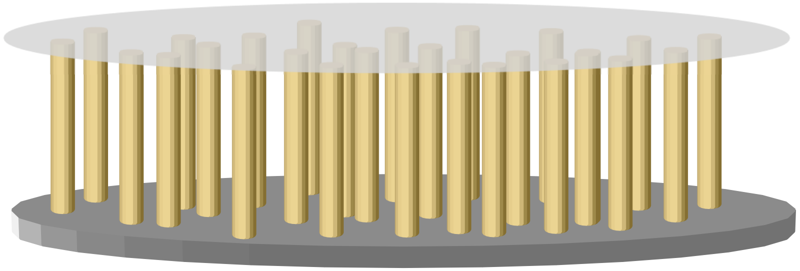
Conclusions

- Distribution of piezoelectric responses and resistivity
- Rod resistivity and d_{33} response are correlated
- Conduction electrons reduce piezoelectric coefficient through reduction of Madelung energy of crystal

Individual



Ensemble



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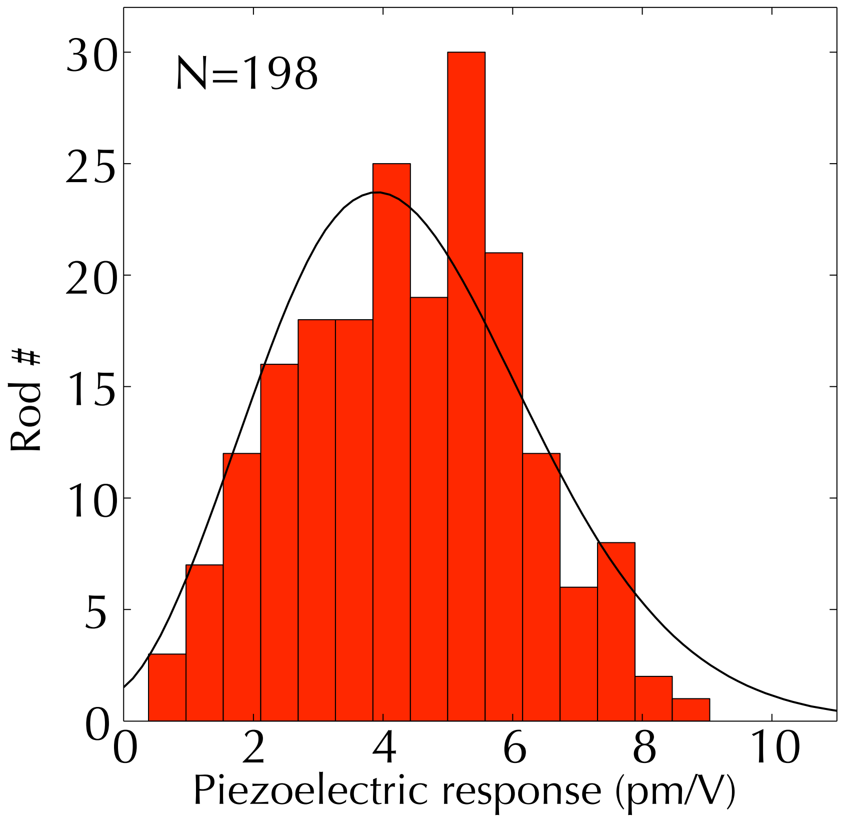
The End

Both coated and uncoated rods have the same piezoelectric response distribution

Bare Rods

4.41 ± 1.7 pm/V



Au Coated Rods

4.1 ± 2.3 pm/V