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Piezoelectric Properties of Solution Grown ZnO Nanocrystals

D. Scrymgeour, J. W. P. Hsu *Sandia National Labs, Albuquerque, NM 87185*

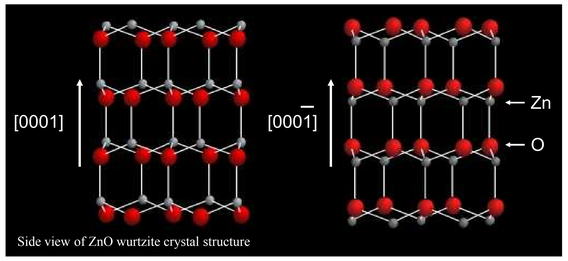
Objective and Motivation:

Solution grown ZnO nanorods were examined by piezoelectric force microscopy (PFM) to determine the orientation and growth direction of the rods from silver substrates. Many important physical properties of ZnO is dependent upon crystal polarity including impurity incorporation, optical and electrical properties, and chemical reactivity.

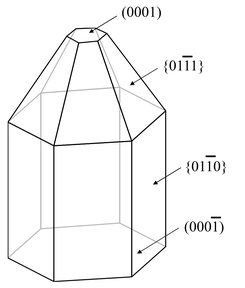
Introduction:

Zinc oxide nanocrystals are grown by solution techniques on highly textured Ag (111) films in patterned arrays. These ZnO nanocrystals form hexagonal crystal rods with diameters of 100-600 nm and heights of 400-1200 nm with their <0001> polar axis perpendicular to the substrate. However, the specific growth direction from the substrate, either along [0001] or [000$\underline{1}$], and hence the crystal polarity, is unclear. A piezoelectric material will develop a strain in linear response to an applied electric field. The piezoelectric coefficient, d_{33}, is defined with respect to the [0001] crystallographic axis and a piezoelectric crystal will respond oppositely for the two polarities.

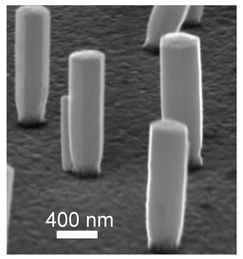
Zinc Oxide Crystal Structure and Morphology



Morphological observations of bulk crystallites formed in solution form a truncated hexagons characterized by a pointed (0001) face and flat (000$\underline{1}$) face. Initial morphological examinations of the ZnO nanorods show a slight truncation near the surface of the silver which might indicate a [000$\underline{1}$] rod orientation from the substrate.



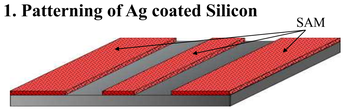
Idealized solution grown ZnO habit
Adapted from Laudise & Ballman, *J. Phys. Chem*, **64**, 688 (1960).



SEM picture of ZnO nanorods

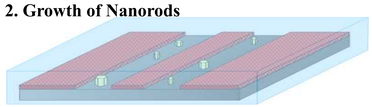
Nanorod Growth:

1. Patterning of Ag coated Silicon



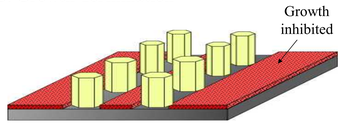
Microcontact printing of $HSC_{10}H_{20}COOH$ self assembled monolayer (SAM) on highly textured (111) Ag coated silicon

2. Growth of Nanorods



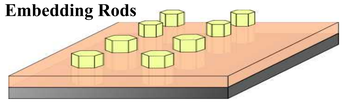
Zinc nitrate ($Zn(NO_3)_2$) and hexamethylenetetramine (HMT, $(CH_2)_6N_4$) in water at 50-60° C for 1-3 hours. Growth inhibited on areas covered by SAM.

3. Growth Termination



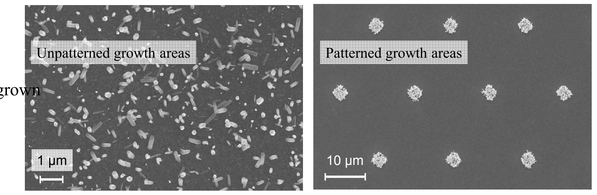
Remove from solution and rinse in water.

4. Embedding Rods



Embedding with Shipley 1811 photoresist and plasma cleaning ($Ar+O_2$) to expose rods. Provides support of rods during PFM measurements.

SEM images of grown nanorods

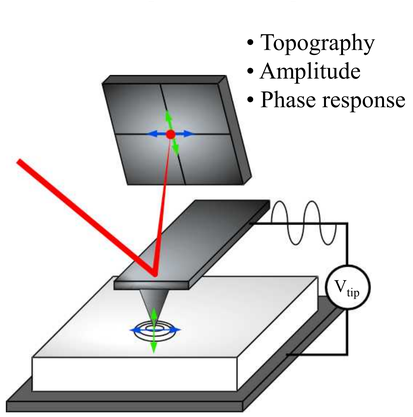


Patterning allows the same individual nanorod to be reliably found with the PFM technique after sample processing, sample rotation, or tip change.

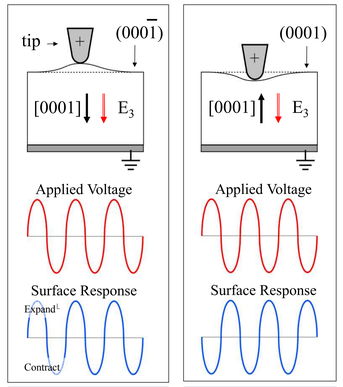
Piezoelectric Force Microscopy (PFM)

In this scanning probe technique, an oscillating voltage is applied to the surface through a conductive tip placed in contact with a piezoelectric material. The applied electric field will cause the material to expand or contract through the piezoelectric effect and the small surface oscillations are measured using a lock-in amplifier. Images of the the amplitude and the phase of the surface oscillation with respect to the applied field are collected.

PFM Experimental Setup



PFM Phase Response



0° phase shift on (000$\underline{1}$) face

180° phase shift on (0001) face

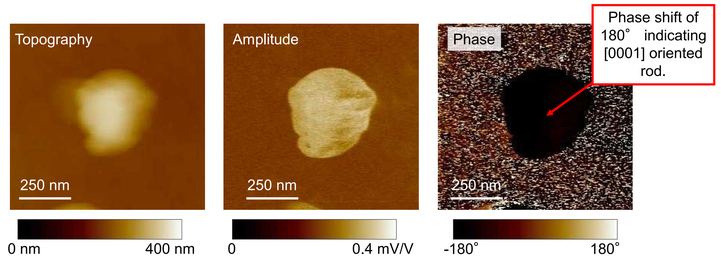
The piezoelectric effect is given as $\varepsilon_3 = d_{33}E_3$ where ε_3 is the strain, d_{33} is the piezoelectric coefficient, and E_3 is the applied field. In bulk ZnO, d_{33} is a *positive* value. This means:

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

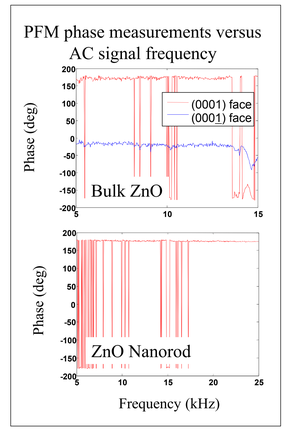
So the relative phase shift of the phase signal (0° or 180°) relative to an oscillating signal indicates the orientation of the material under the tip.

Determining Rod Orientation:

To determine orientation, the rods were examined by PFM. To verify orientation, these results were compared to a bulk single crystal of vapor phase grown ZnO crystal (5x5x.5mm). The orientation of the bulk crystal was determined by 4 different techniques: Etching experiments, anomalous dispersive x-ray diffraction, piezoelectric effect using a d_{33} meter, and PFM Measurements



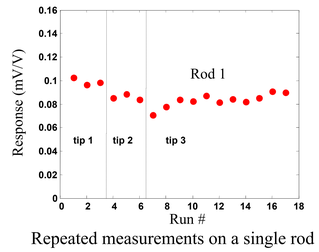
PFM images of single embedded ZnO nanorod



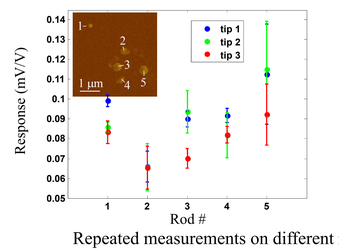
Over 100 individual rods were examined by the PFM technique. All measured rods showed a phase shift of 180º indicating rods grow from the surface in the [0001] direction. This contrasts with the morphological investigations.

Piezoelectric Amplitudes :

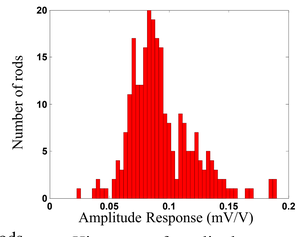
There was a variation of measured amplitudes among different rods, which do not correlate to any of the physical dimensions, individual samples, or growth conditions. The amplitude measurements on individual nanorods were repeatable, which indicates that the variability is not an artifact.



Repeated measurements on a single rod



Repeated measurements on different rods



Histogram of amplitude response

Response	Unelectroded	Electroded
Quartz	15.3 ± 3.6 μV/V	± μV/V
$LiNbO_3$		
ZnO Bulk	16.5 ± 8.6 μV/V	6.38 ± 3.4 μV/V
Zno Nanorod	93.4 ± 26.8 μV/V	NA

The lack of strong correlation to physical dimension indicates another factor is determining the measured response. Since the presence of conductivity can diminish the observed piezoelectric response, the conductive properties of individual rods will be examined next. Comment on amplitudes.

Conclusions:

It was determined by PFM that solution grown ZnO rods growing from silver surfaces are oriented (0001). The amplitudes of oscillation showed variation between rods that did not correlate strongly with physical dimension or growth condition indicating that the variability is a factor of another material property, perhaps the conductivity.

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