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nFrancisco,Omaha,Orlado,Rayleigh,SantaClara,Chicago,Philadelphia,Un
gdom,Baltimore,SanAntanio,Dubai,Hyderabad,Bangaluru and Mumbai

omparison of ZnMgO/ZnO Coaxial Cor ell Structures with ZnO Nanorods for U detection and Gas Sensors

Abdiel Rivera, Anas Mazady, Mehdi Anwar

University of Connecticut
Storrs, CT

UCON
School of Engin

ZnO Properties & Applications

Property	Value
Lattice parameters at 300 K (nm)	a_0: 0.32495 c_0: 0.52069
Density (g cm^{-3})	5.606
Stable phase at 300 K	Wurtzite
Melting point (°C)	1975
Thermal conductivity	0.6, 1-1.2
Linear thermal expansion coefficient	a_0: 6.5×10^{-6} c_0: 3.0×10^{-6}
Static dielectric constant	8.656
Refractive index	2.008, 2.029
Energy bandgap (eV)	Direct, 3.37
Exciton binding energy (meV)	60
Electron effective mass	0.24
Electron Hall mobility, n-type at 300 K (cm^{2}V^{-1}s^{-1})	200
Hole effective mass	0.59
Hole Hall mobility, p-type at 300 K (cm^{2}V^{-1}s^{-1})	5 - 50

Applications

UV-Diode[1]

Gas Sensor[2]

Bio-Sensors[3]

Solar Cells[4]

Nano-generators[5]

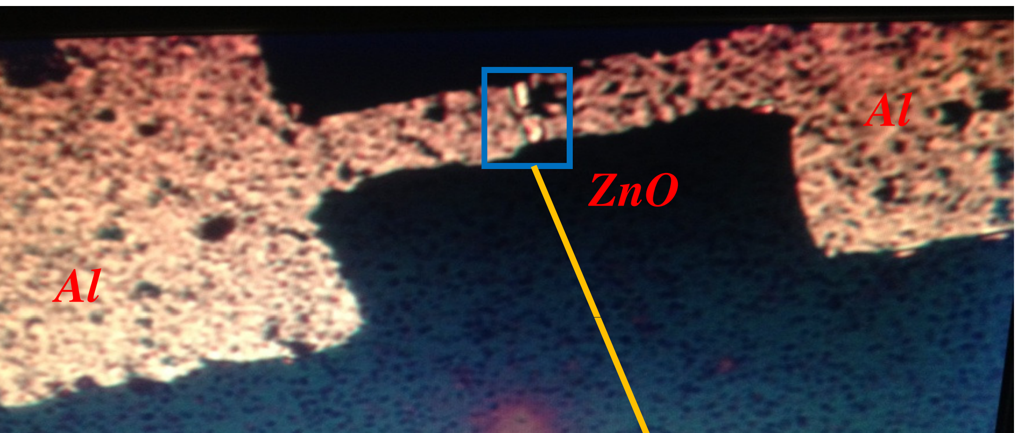
FETs[6]

Thermoelectric Applications[7]

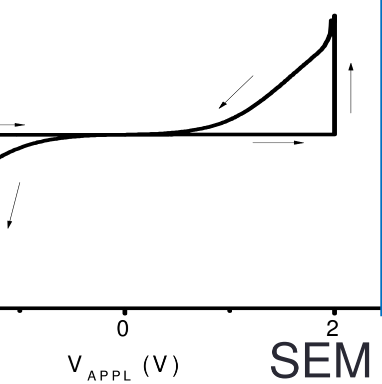
- 1-Min-Chang Jeong (2006)
- 2-Sachindra Nath Das (2010)
- 3- A. Wei (2006)
- 4- O. Lupan (2010)
- 5-Seung Nam Cha (2010)
- 6- G. F. Boesen (1968)
- 7-Chul-Ho-Lee (2009)

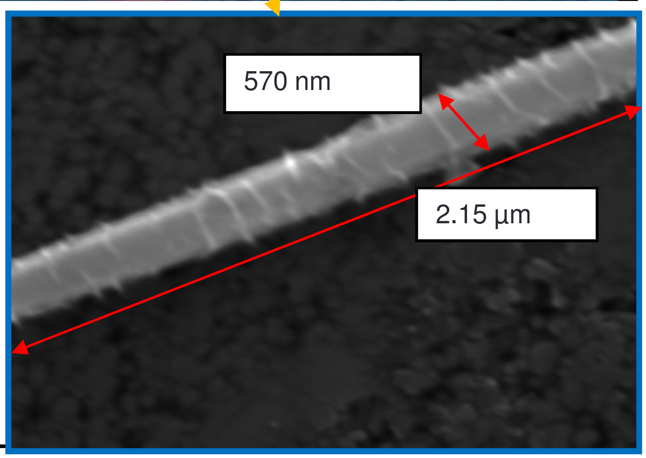
ications Demonstrated by our group

mory Device



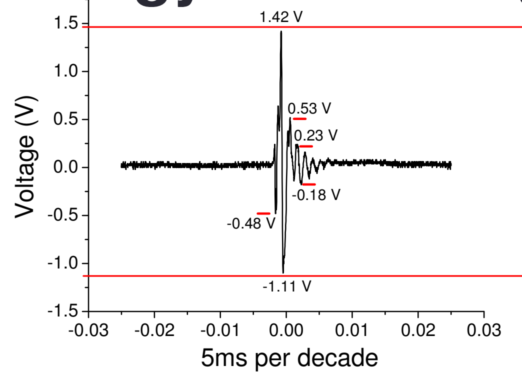
Microscope

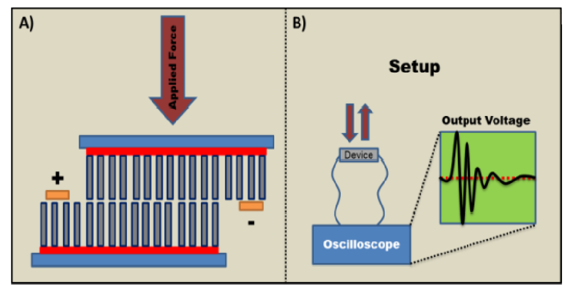




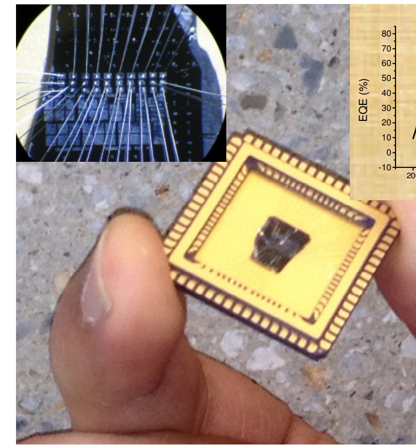
SEM Image of ZnO horizontal NW

Energy Harvesting

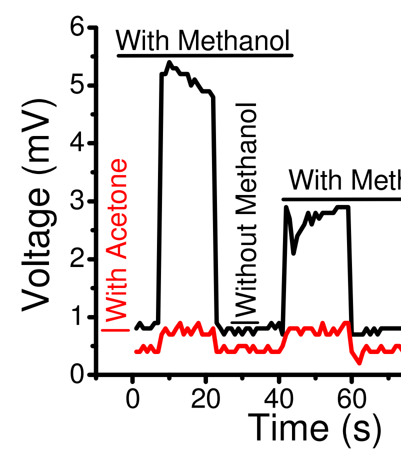




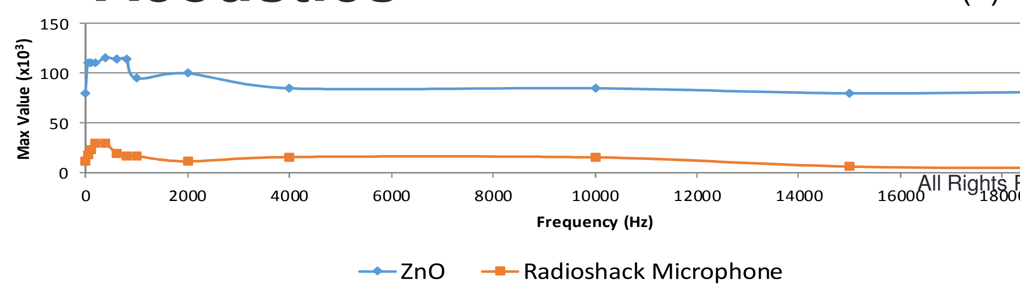
Deep UV Det



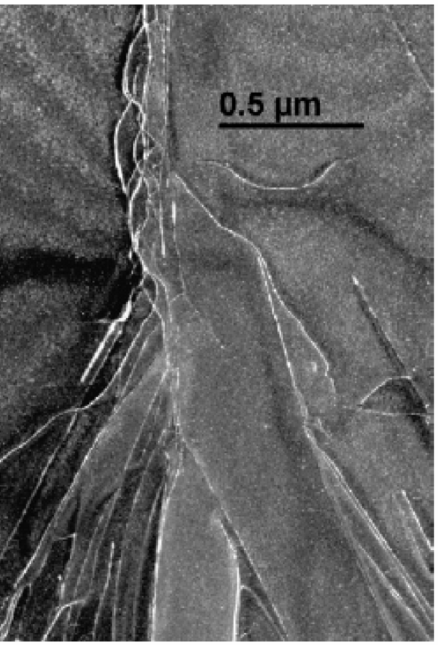
Gas Sensi



Acoustics

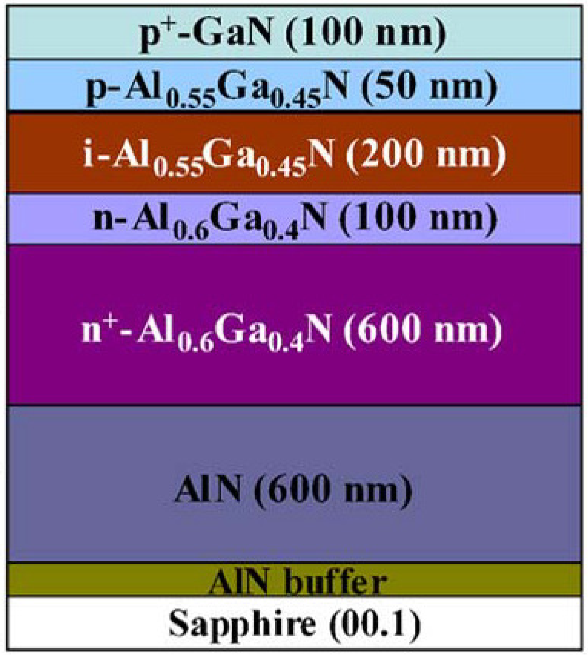


erial Choice



age showing dislocations in AlGaN
t et al. , J. Crystal Growth 310 (2008)

using $Al_xGa_{1-x}N$-based
generate dislocations and
e to lattice and thermal



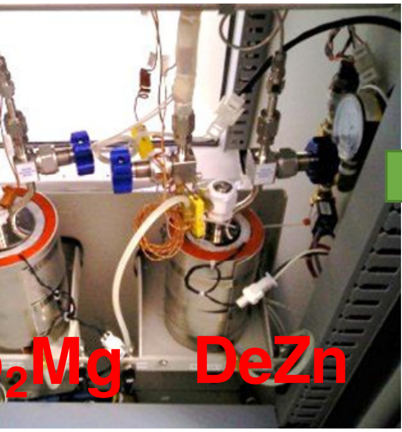
Device cross section of a AlGaN-based uv detector Cicek *et al.* (Razeghi's group) [Optics Lett. Vol. 37, No. 5, Mar 1, 2012])

- Lack of free standing substrates for III-N films
- Layered structure introduces added complexity to the growth process

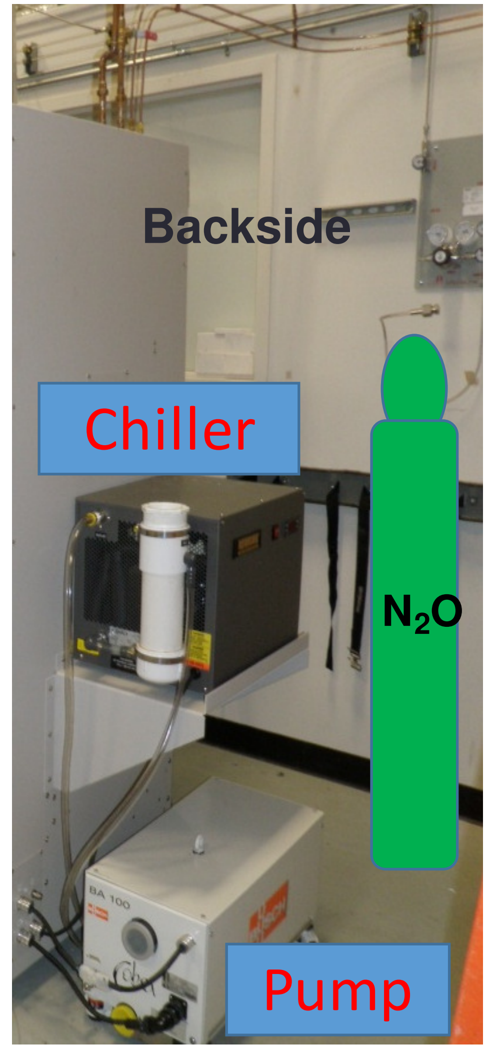
ZnO Features

- Large direct bandgap er
  ~3.37 eV
- The direct bandgap of Z
  can be engineered to la
  values by doping with M
- Capability to be grown o
  cheap Si substrates
- Piezoelectric property a
  biocompatibilty

MOCVD Growth

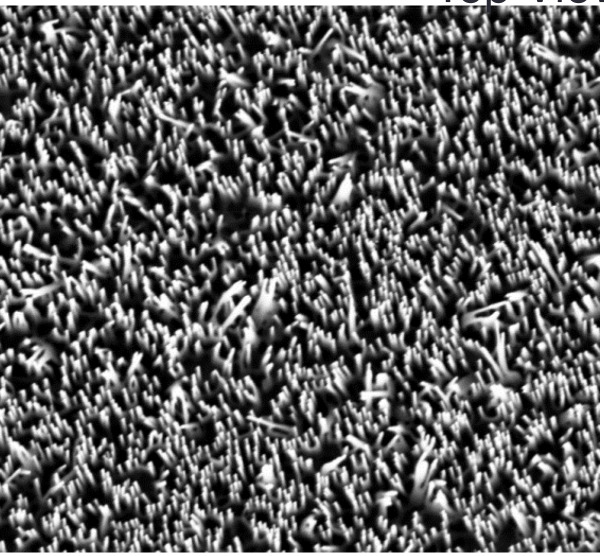


- First Nano EasyTube 3000
- 3 zone resistance furnace for temperature upto 1100 ^{0}C
- 5” quartz reaction chamber
- Base pressure <50 mTorr

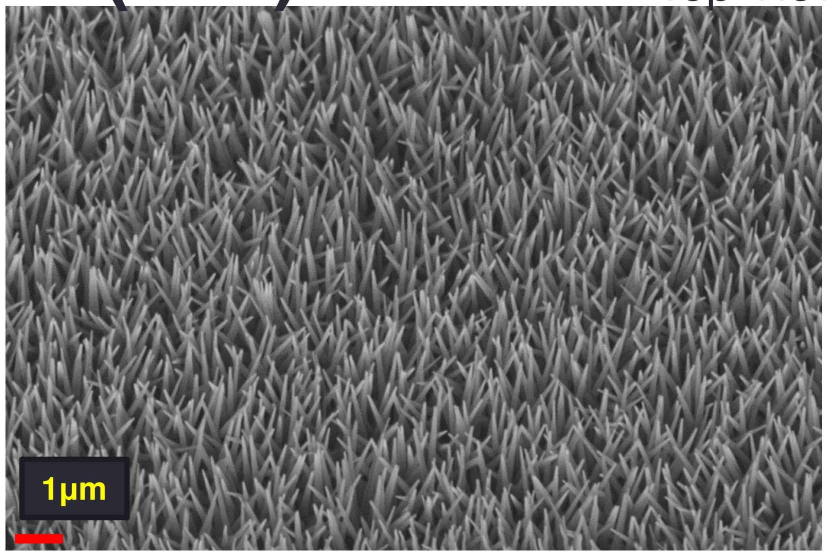


aN	p-Si (100)	p-Si (111)
• Diameter: 20 – 40 nm • Length: 0.70 – 1.00 µm	• Diameter: 150 – 200 nm • Length: 1.00 – 1.50 µm	• Diameter: 9 • Length: 1 –

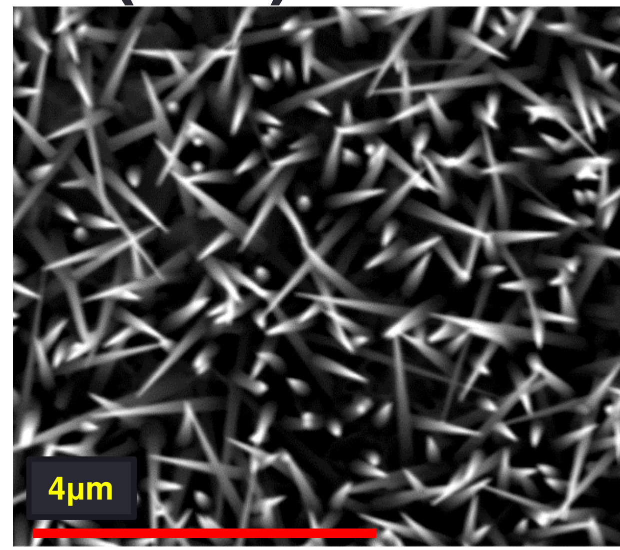
Top View



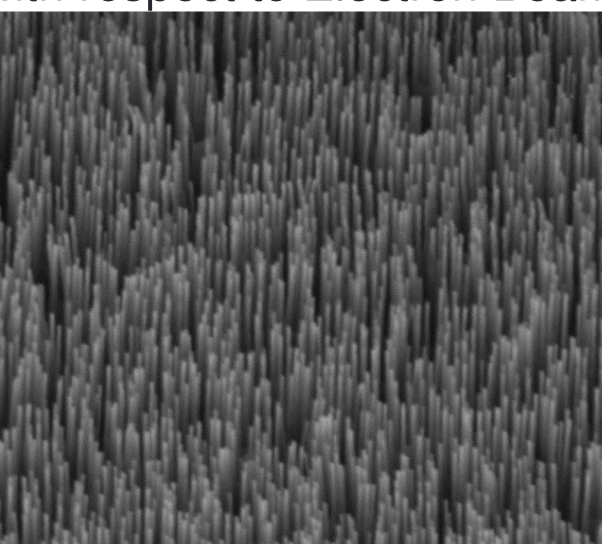
Top View



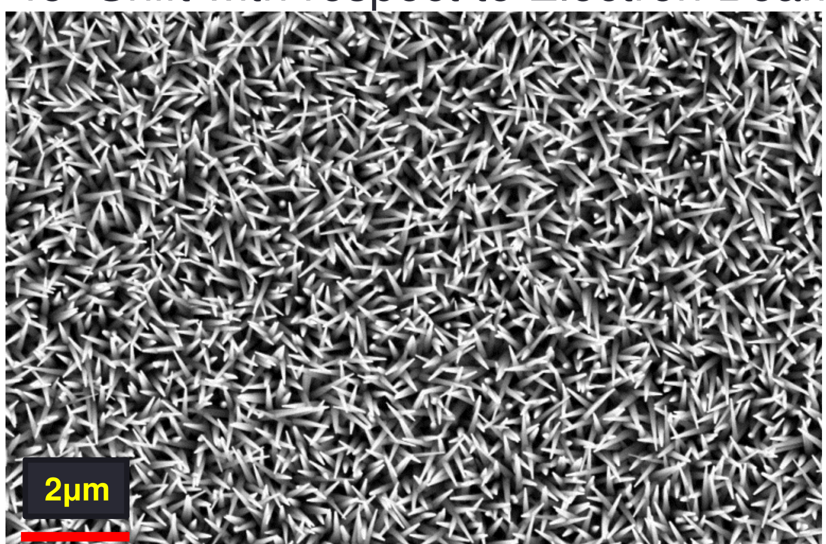
T



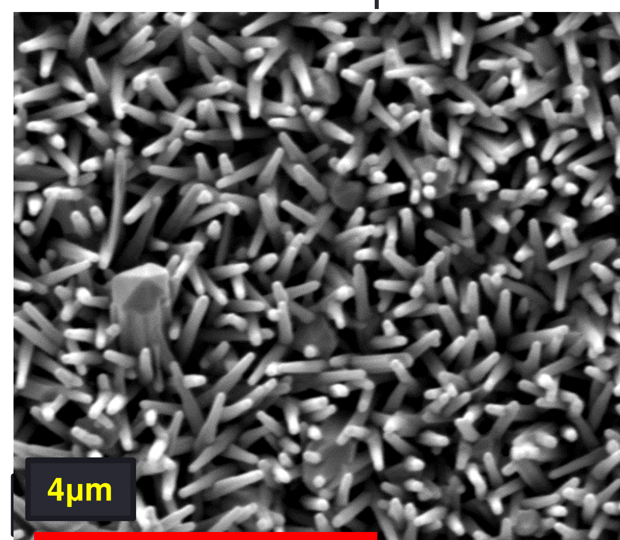
with respect to Electron Beam



45˚ Shift with respect to Electron Beam



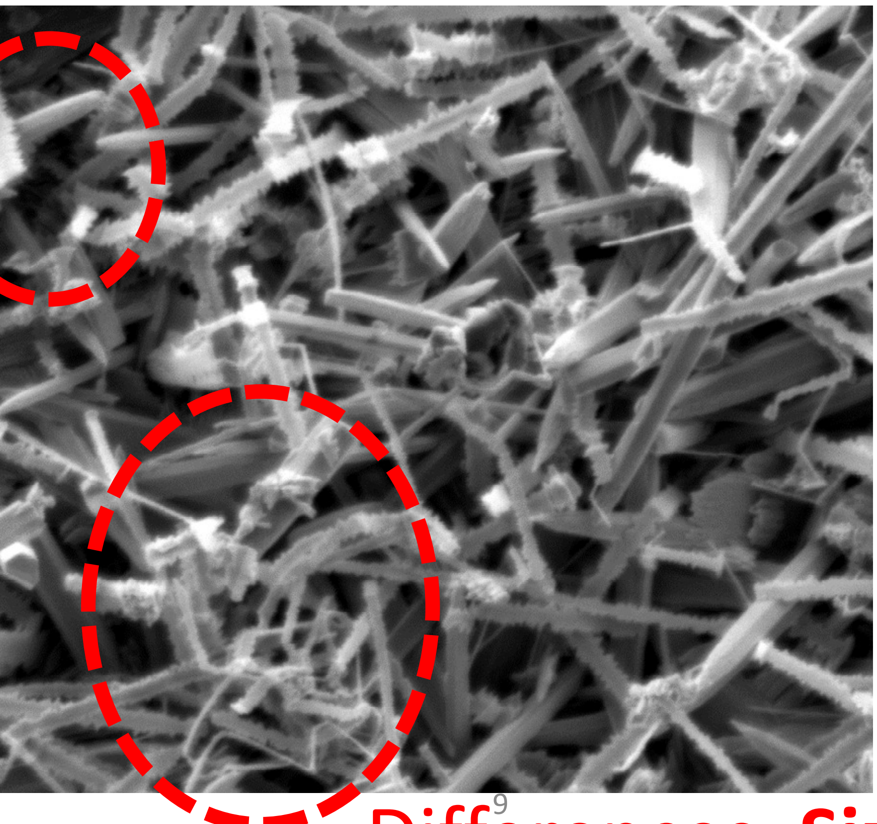
45˚ Shift with respect to Elec



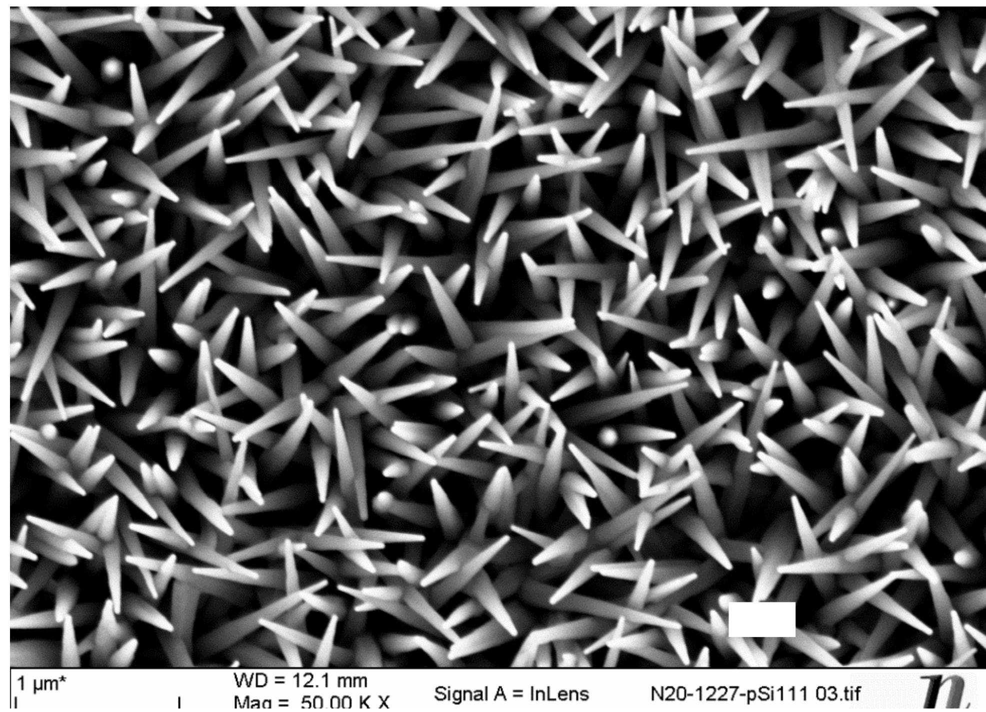
a et al., “A Comparison of ZnO Nanowires and Nanorods Grown Using MOCVD and Hydrothermal Processes”, *J. Electron. Mater.,* Vol. 42,
1, 2013.

nparison of Au Catalyst assisted/No Catalys sted: Growth Direction and Alignment

talyst assisted growth

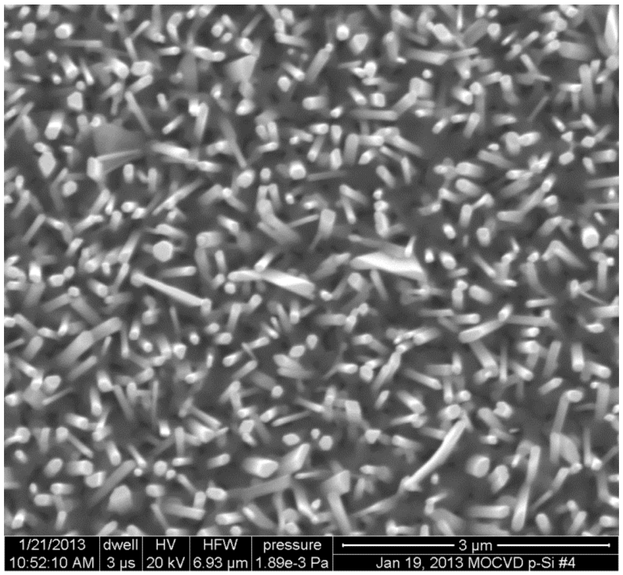


Growth using MOCVD witho catalyst



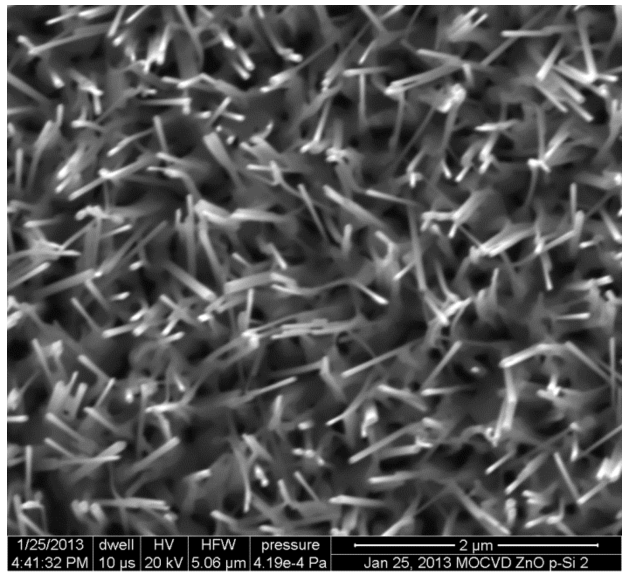
Differences: **Size** (length & diameter), **Orientation**, **Gold Particles**, **Tip Shape**.

Structural Quality Vs. Annealing



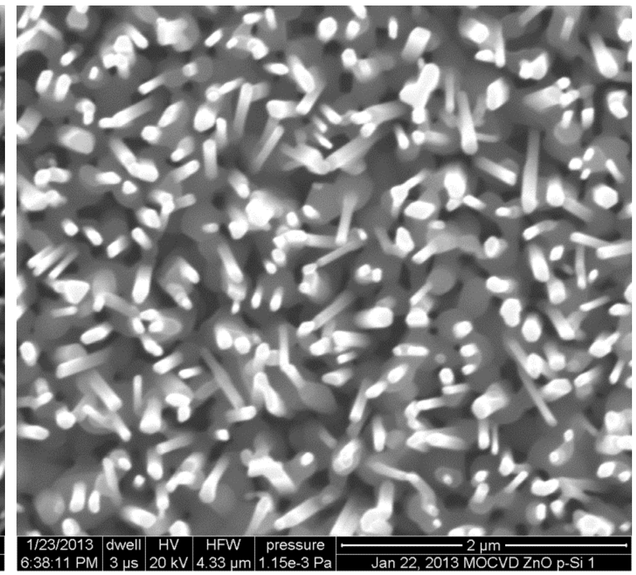
ETA 635

- ZnO epitaxy annealed at 635C
- NWs are NOT annealed



ETA 800

- ZnO epitaxy annealed at 800C
- NWs are NOT annealed



ENTA 800

- ZnO epitaxy annealed at 800C
- NWs are annealed at 800C

- Annealing the epitaxy does not affect the ZnO NWs morphology because the NWs are already lattice matched with the ZnO epitaxy
- Annealing the NWs decreases the surface area to volume ratio which may be related to the decrease in c-lattice constant of the NWs

yet al., "**Effects of Annealing on Structural and Optical Properties of ZnO Nanowires**", *Materials Research Society (MRS) Spring Meeting &*
, April 21-25, 2014. and to be published on MRS Proceedings

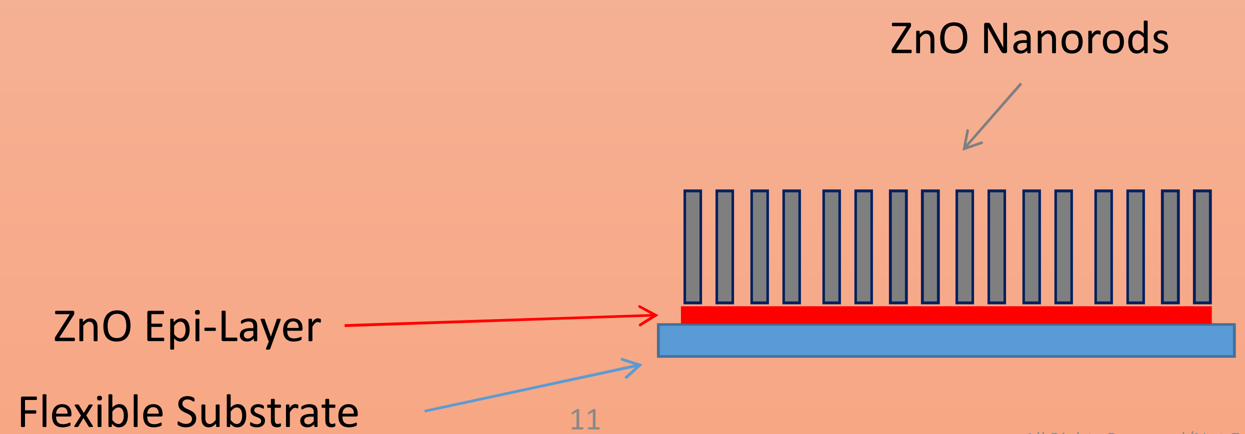
nO Nanorods via Hydrothermal Synthesis

2 Step Epi-Layer

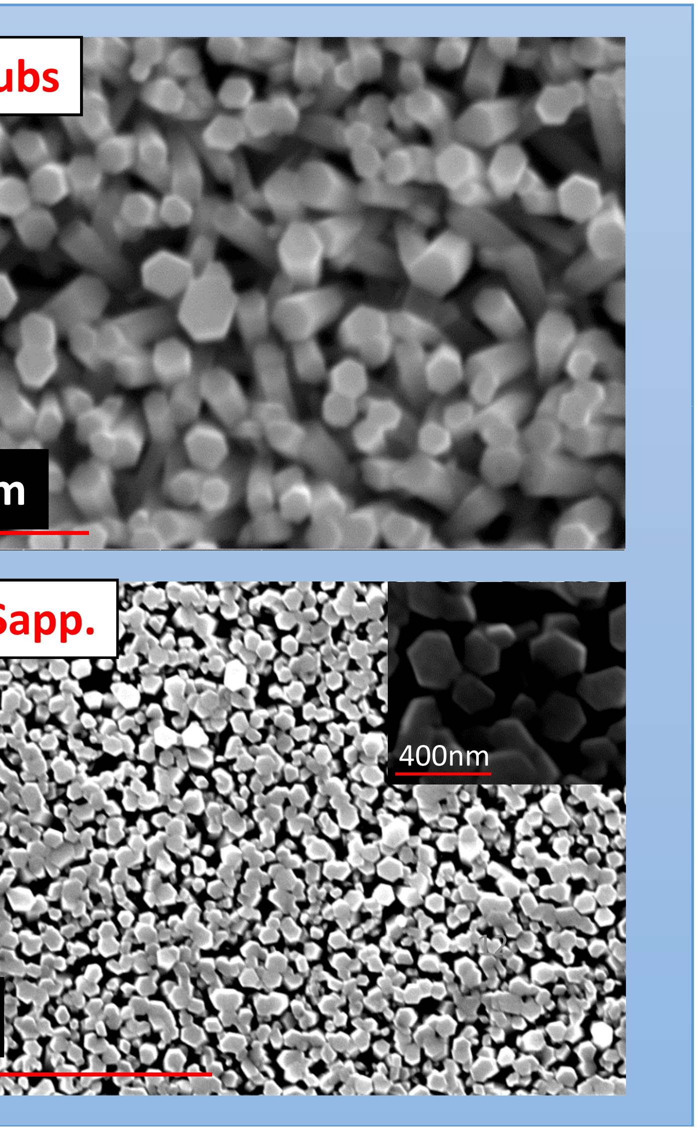
Solution:	Spin	Suspend sample in:
50mL Methanol	500 rpm, 5 sec	0.1M $Zn(NO_3)_2$
0.09g $Zn(CH_3COOH)_2$	3000 rpm, 30 sec	0.1M HMTA
0.12g KOH	10min at 60˚C	60min at 90˚C

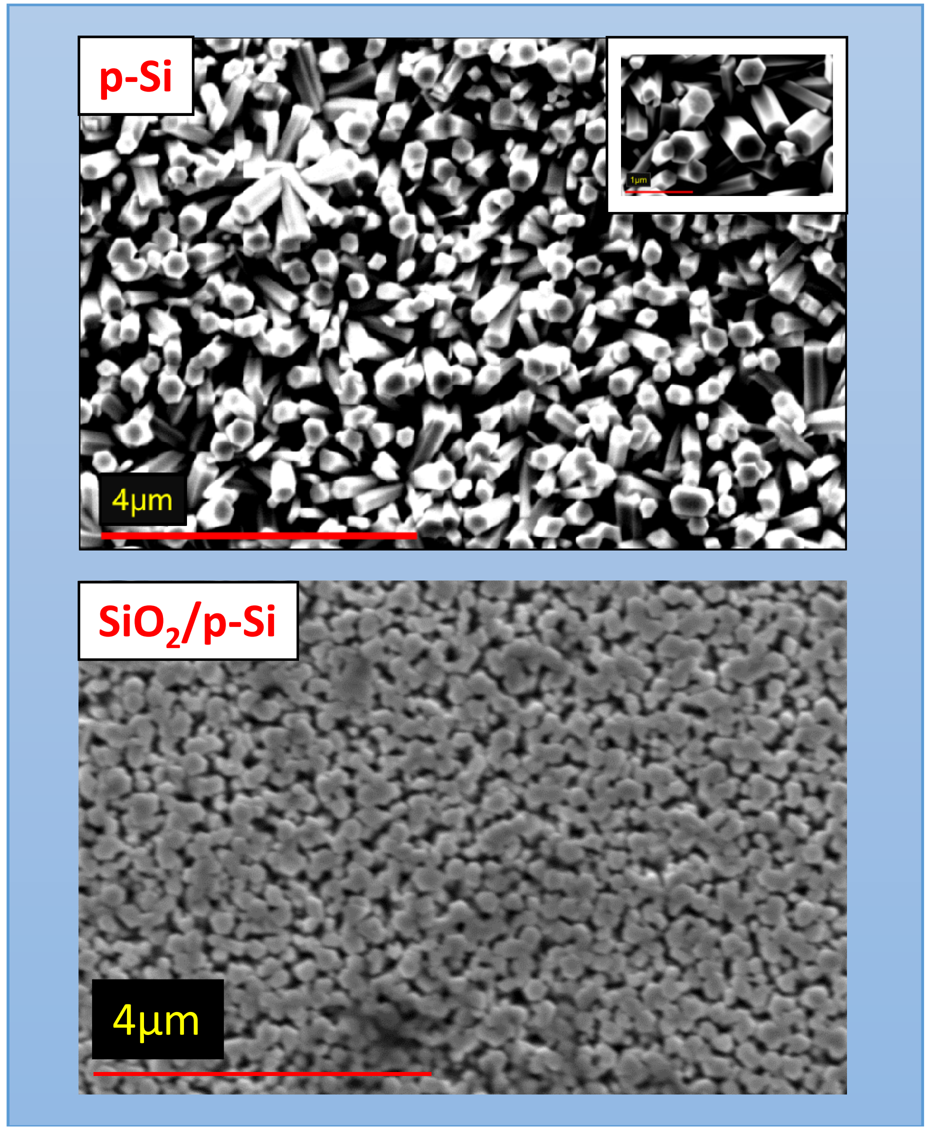
Hydrothermal

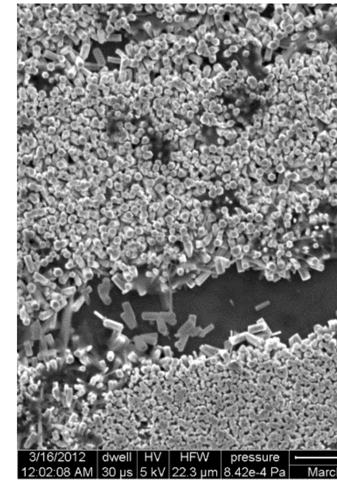
Suspend sample in:
0.1M $Zn(NO_3)_2$
0.1M HMTA
7h at 70˚C



M of ZnO Nanorods grown on Flexible Substra
p-Si, GaN and SiO_2/p-Si



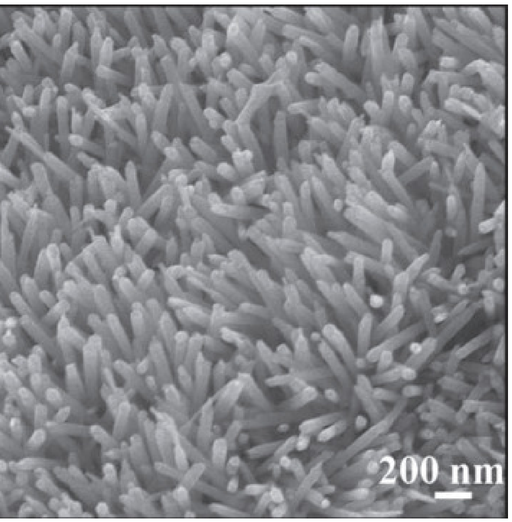




ZnO NRs with see
Chemical Bath De

Abdiel Rivera et al
Comparison of ZnO
Nanowires and Nan
Grown Using MOC
Hydrothermal Proc
Electron. Mater., Vo
5, pp. 894-900, May

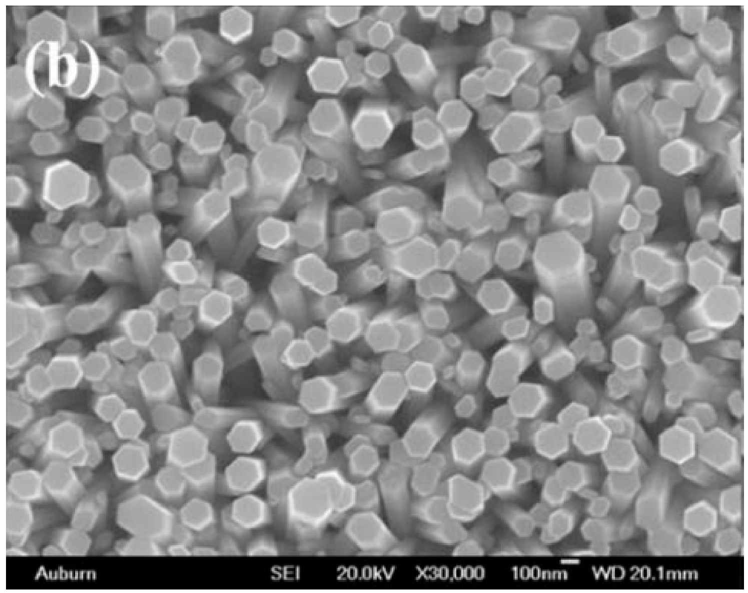
Reported Work



wn on paper using
rmal

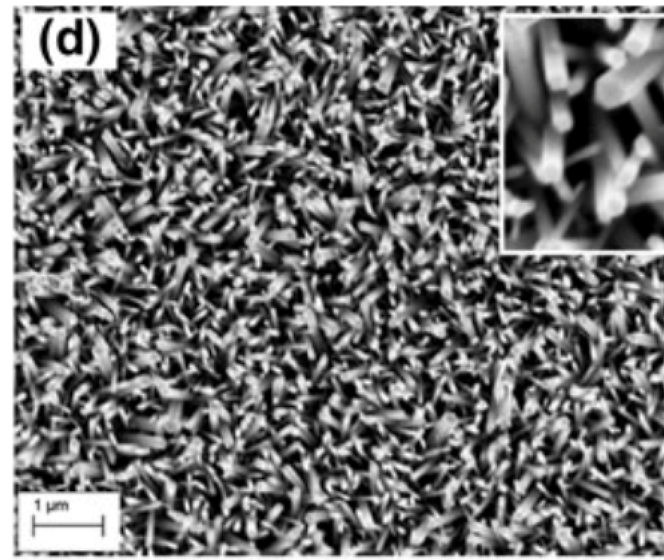
hickness: 60-70nm
ength: 1.5um

adi et al Adv. Mater. 22, (2010) 4059



ZnO grown on flexible polyimide film grown via chemical solution

Thickness: 100-250nm
Length: 1.5um



ZnO grown on flexible substrat
using CBD, with seed layer dep
via RF sputtering

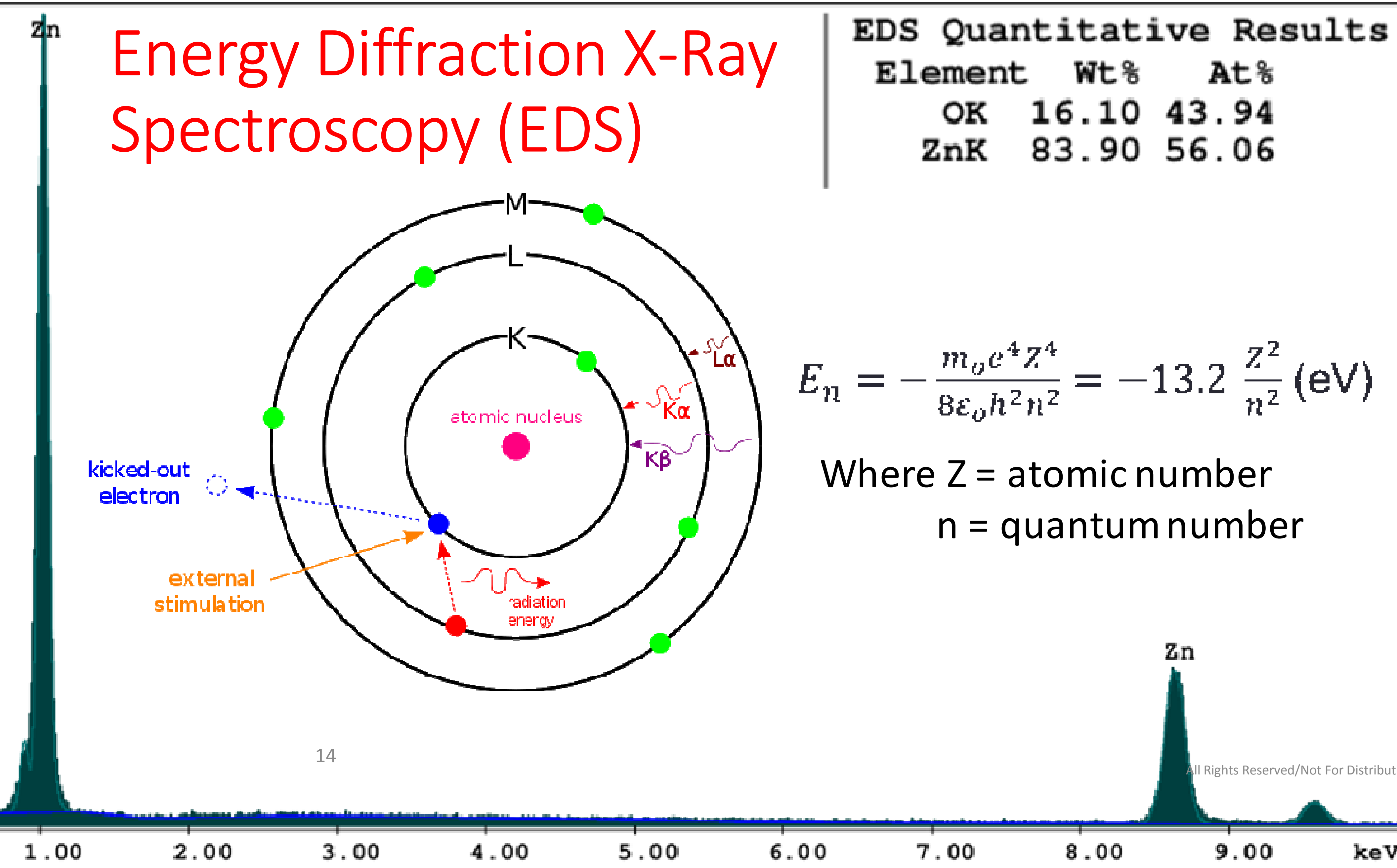
T.A. Nirmal et al J. Nanopart Res (2013)

H. Ahn et al Electrochemical and Solid-State Lett. 13, (11) (2010) J125

Energy Diffraction X-Ray Spectroscopy (EDS)

EDS Quantitative Results

Element	Wt%	At%
OK	16.10	43.94
ZnK	83.90	56.06

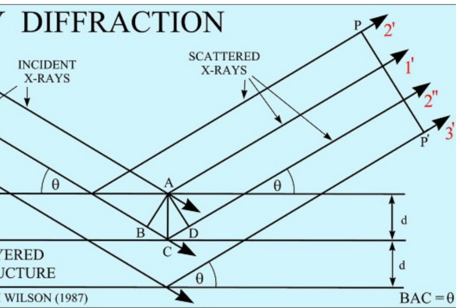


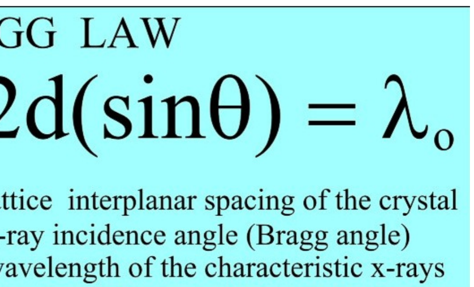
$$E_n = -\frac{m_o e^4 Z^4}{8\varepsilon_o h^2 n^2} = -13.2\,\frac{Z^2}{n^2}\,(\text{eV})$$

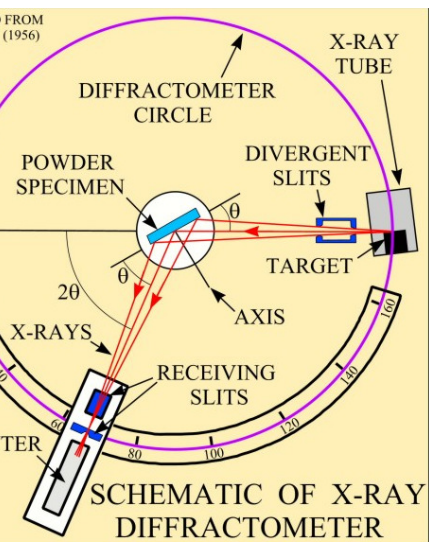
Where Z = atomic number

n = quantum number

y Diffraction







Calculate the *c* & *a*-lattice constant Wultzite crystals

Eq from : "Elements of X-Rays Diffraction" by Cullity, page 310

$$sin^2\theta = \frac{\lambda^2}{4}\left[\frac{4}{3}\left(\frac{h^2+hk+k^2}{a^2}\right)+\frac{l^2}{c^2}\right]$$

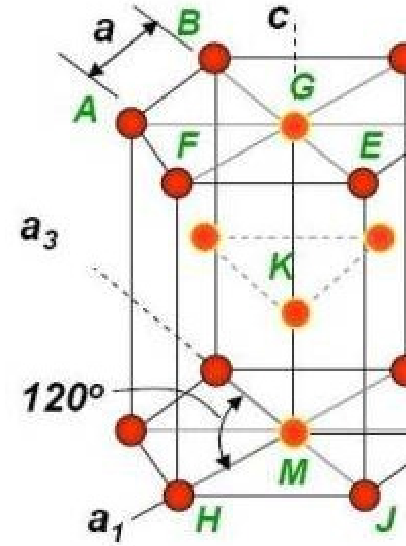
Calculation for[1]

$$\theta_1 = \frac{34.38}{2} = 17.19;\ \theta_2 = \frac{34.34}{2} = 17.17$$

$$\lambda = 1.5427x10^{-10};\ h = k = 0;\ l = 2;$$

λ correspond to CuK_α

$$c_1 = 5.2199x10^{-10};$$
$$c_2 = 5.2258x10^{-10}$$

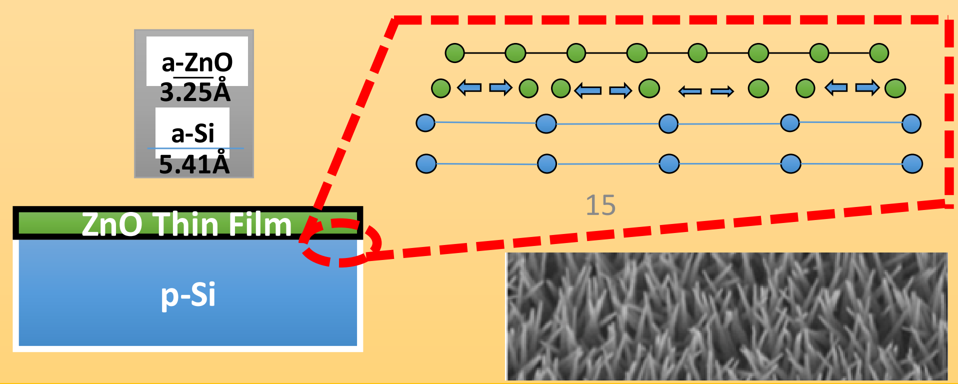


ZnO Wurtzite Atoms A

Stress-Strain Calculatio

$$\epsilon_\perp = \frac{c_{grown} - c_0}{c_0};\quad \epsilon_\parallel = \frac{a_{gr}}{}$$

Lattice Mismatch of seed layer with substrate



Lattice Mismatc

$$\frac{a_{ZnO} - a_{Si}}{a_{Si}} =$$

$$\frac{3.25 - 5.41}{5.41} = -0.$$

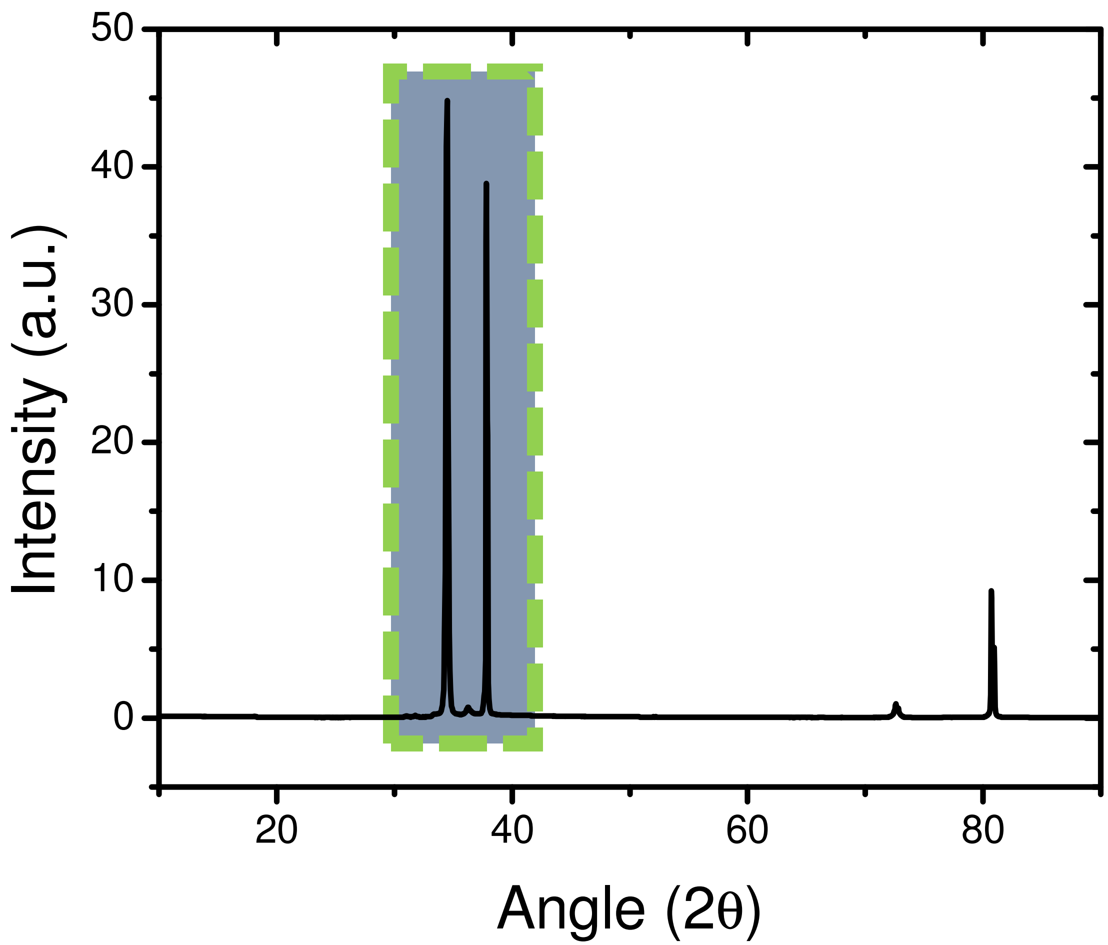
Tensile Strain

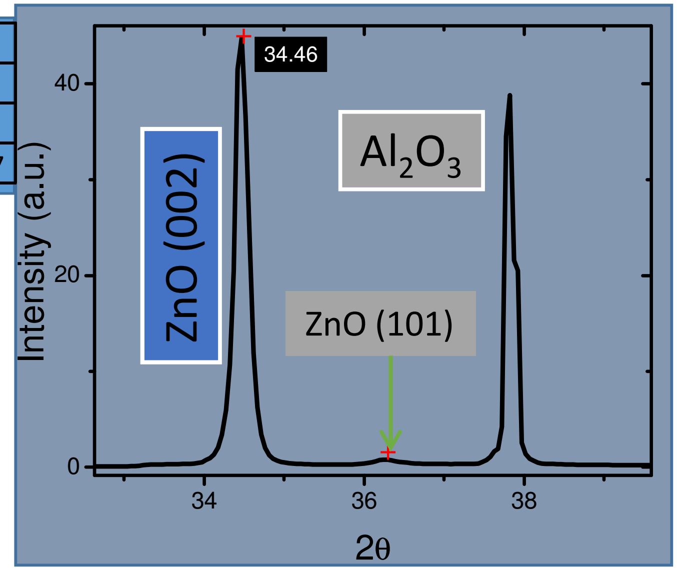
X-Ray Diffraction – ZnO/Al_2O_3

FWHM = 0.0830˚(θ)
c-lattice = 5.2011 Å

Substrate	Growth Method	c-lattice	FWHM	Reference
GaN	Electrodeposition		0.09˚(θ)	Lupan et al. Adv. Mater. 2010, 22, 3298–3302
GaN	CVD	5.203Å		Tsao et al. Appl. Phys. Lett. 92, 203110 (2008)
GaAs	MOCVD	5.216Å	0.323˚(θ)	Lee et al. Acta Materialia 52 (2004) 3949-3957

Taken using Brunker D8 Advance CuK (λ = 1.54 Å) line at Room Temperature





By examining the intensity of P_{002} = 45.28 vs. P_{101} = 1.0617, the ratio $\frac{P_2}{P_1} = 0.0234\ or\ 2.34\%$.

Calculate c-lattice constant

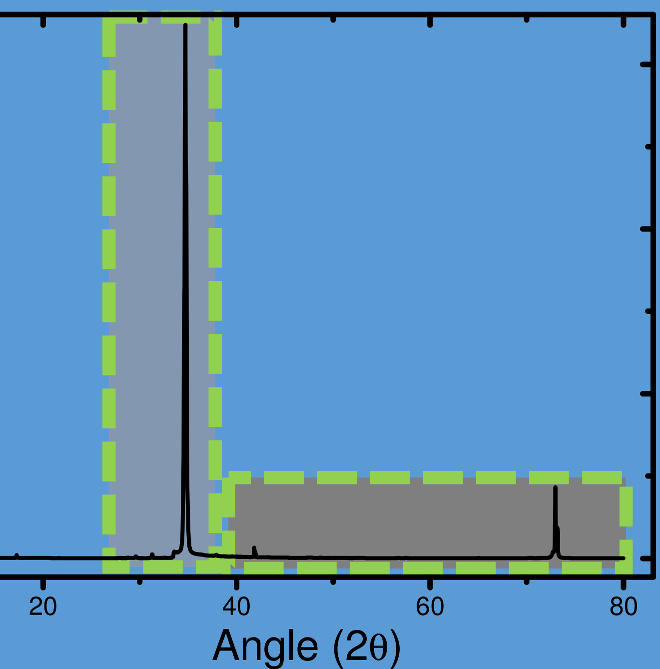
$$sin^2\theta = \frac{\lambda^2}{4}\left[\frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2}\right]$$

$$\theta_1 = \frac{34.46°}{2} = 17.23°\ \lambda = 1.5406x10^{-10}$$

$$h = k = 0; l = 2$$

ZnO c-lattice = 5.206Å
(JCPDS card No. 361451)

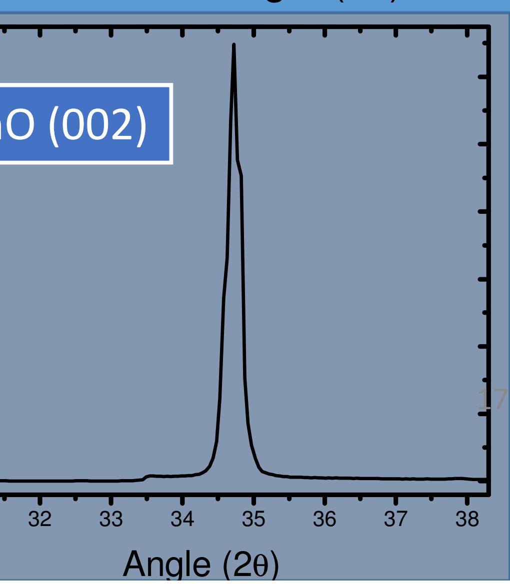
Ray Diffraction

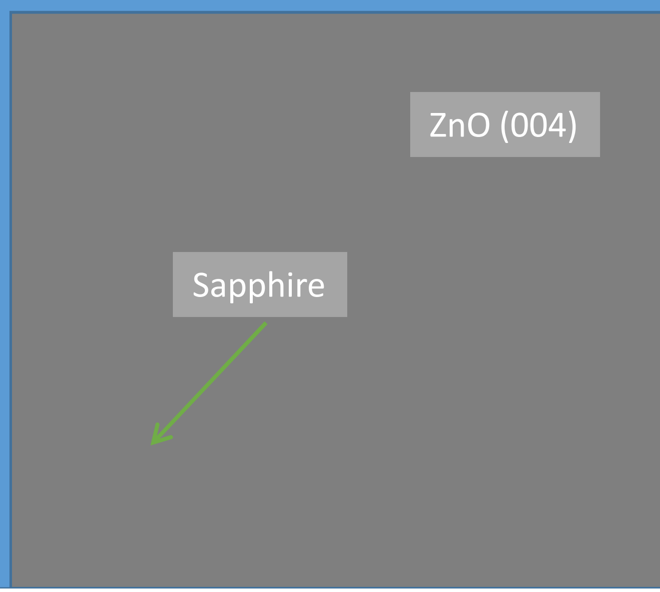


Diffraction Peak for ZnO (002)
Confirming Vertical Alignment

ZnO/u-GaN

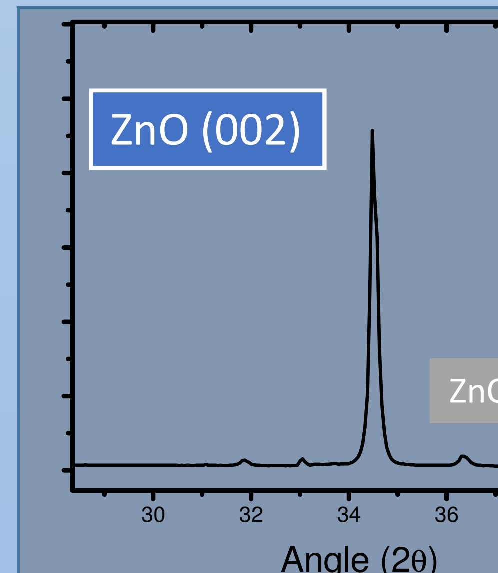
FWHM = 0.0497˚(θ)
c-lattice = 5.1838 Å

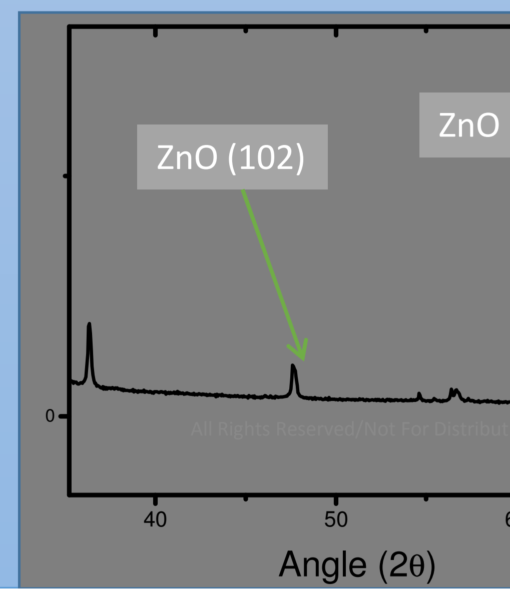




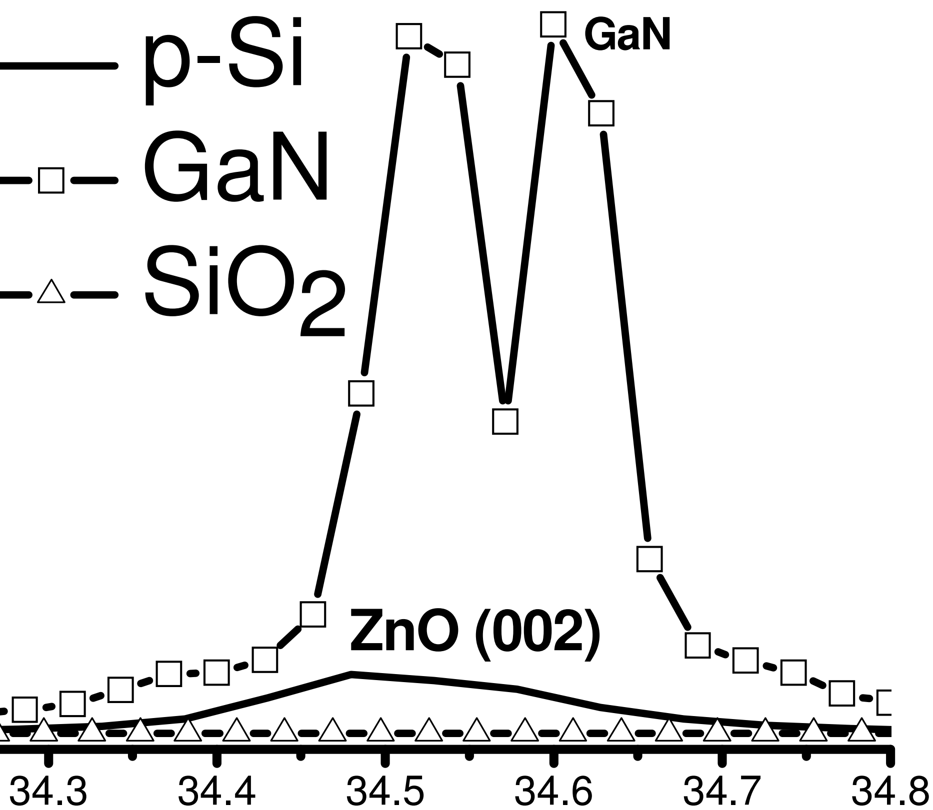
p-Si (100)

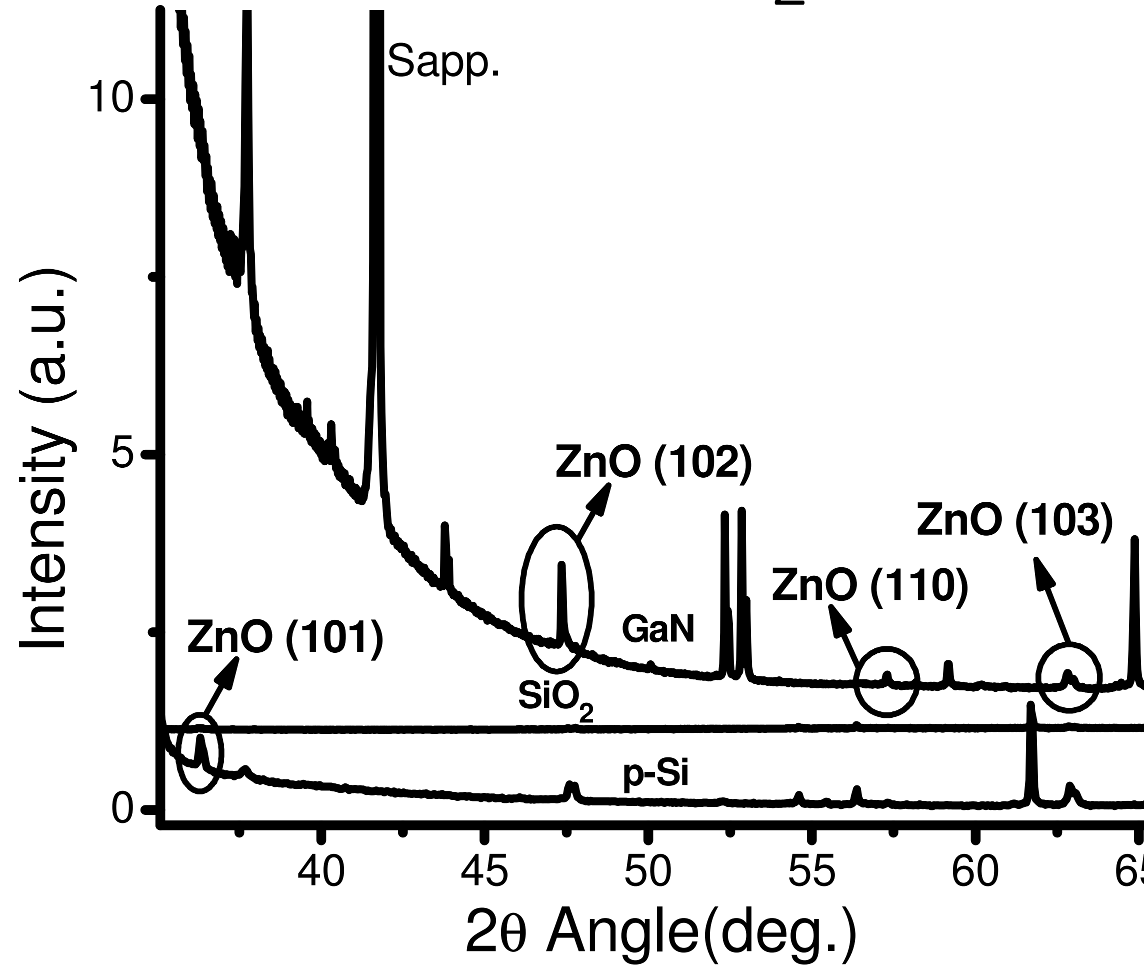
FWHM = (
c-lattice =





XRD – ZnO NRs on p-Si, GaN and SiO_2

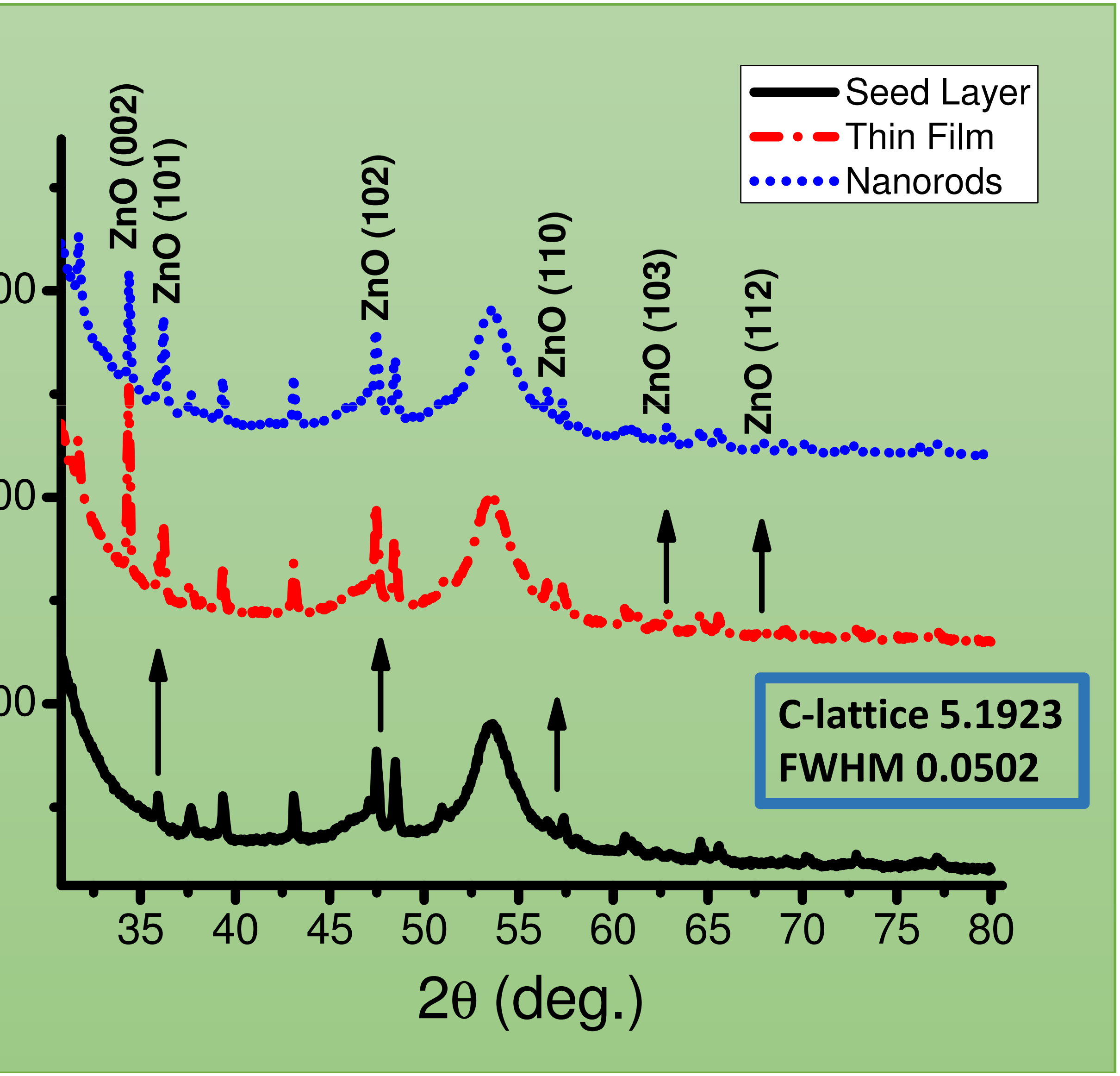


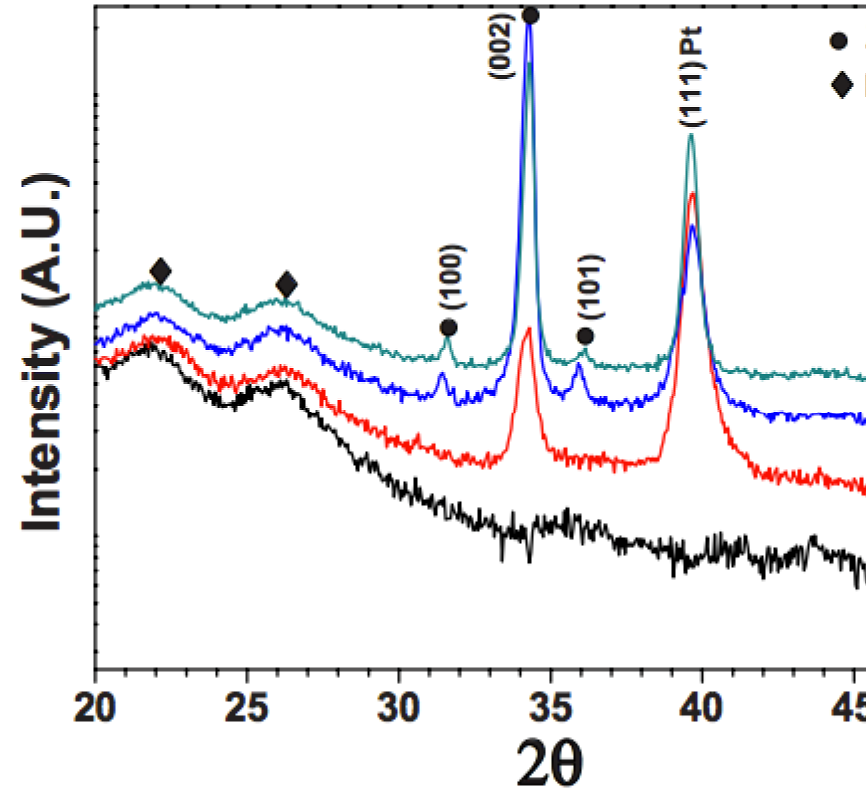


	p-Si	GaN	SiO_2
c-lattice (Å)	5.1971	5.1942	5.19
FWHM 2θ (deg.)	0.0591	0.052	0.0776

a et al., "A Comparison of ZnO Nanowires and Nanorods Grown Using MOCVD and Hydrothermal Processes", *J. Electron. Mater.,* Vol. 42,
1, 2013.

XRD – ZnO NRs

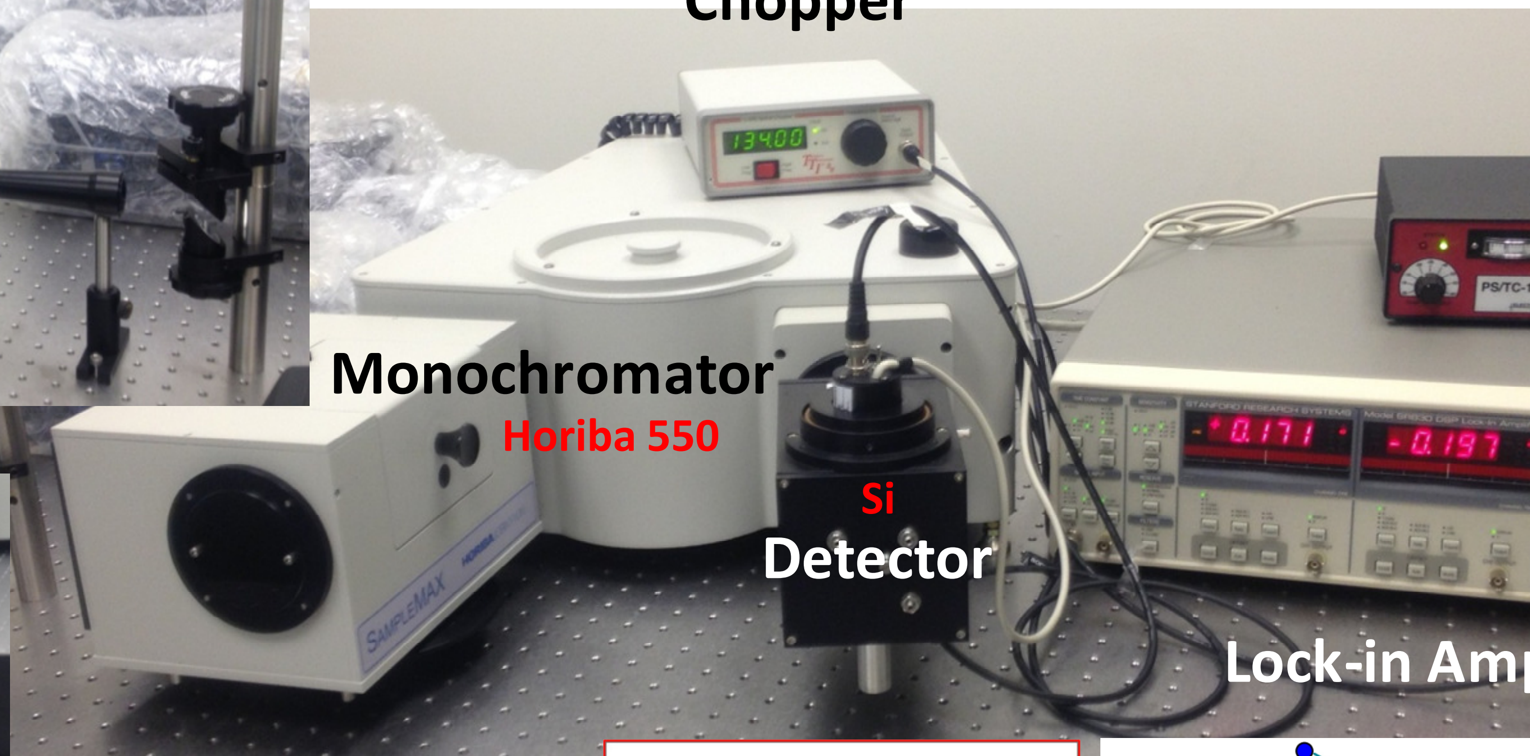


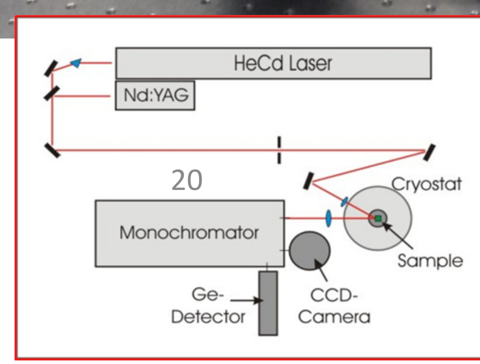


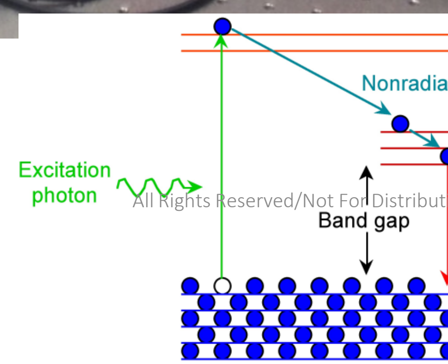
XRD of a) postannealed ZnO NRs, b) as-dep
c) ZnO seed layer on Pt electrode substrate
substrate

H. Ahn et al Electrochemical and Solid-State Lett. 13, (11)

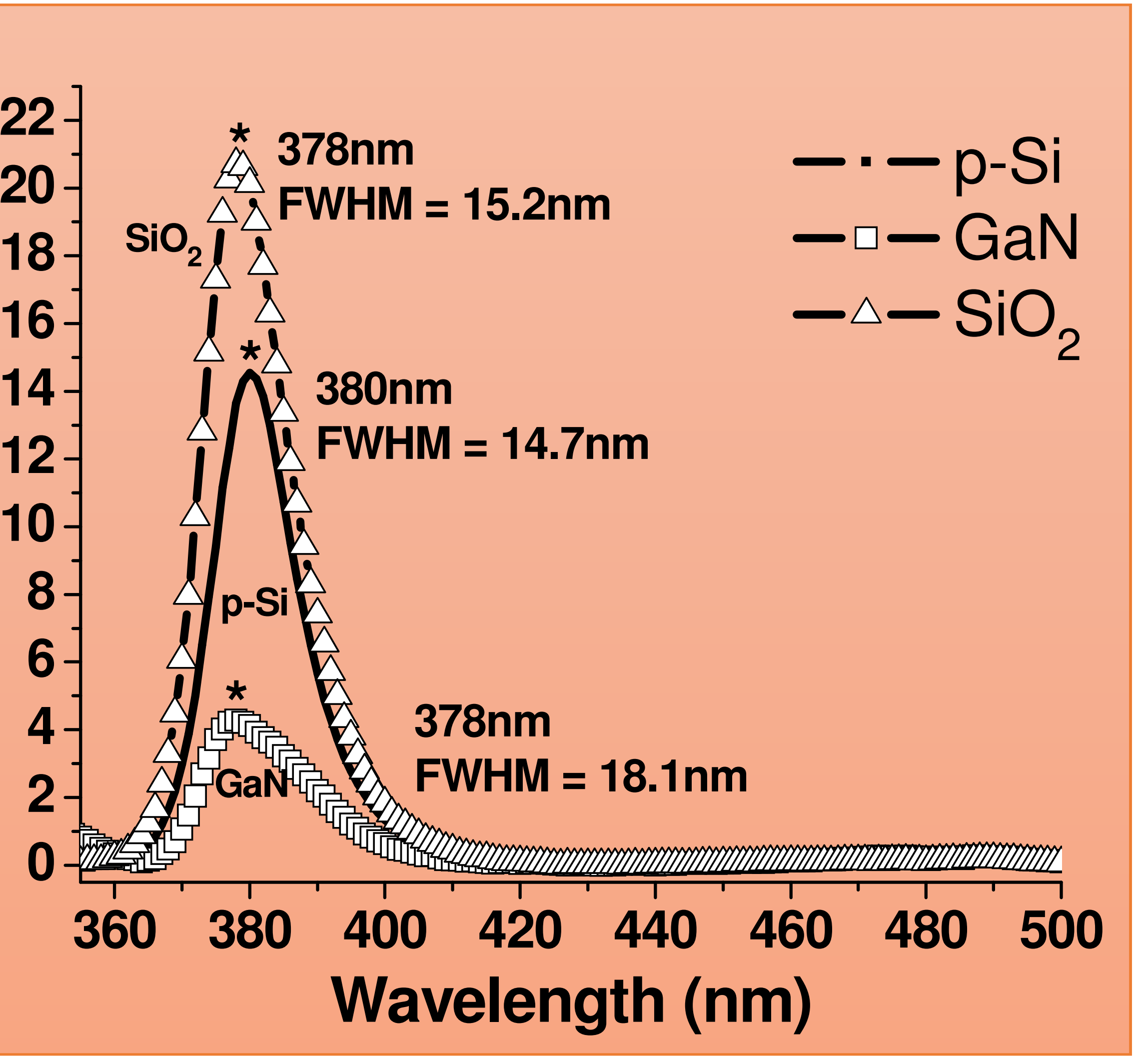
Photoluminescence (PL) Measurement Setup







Photoluminescence (PL)



<u>FWHM</u>

SiO_2

15.2286 nm

p-Si

14.6932 nm

GaN

18.1446 nm

378 – 381nm

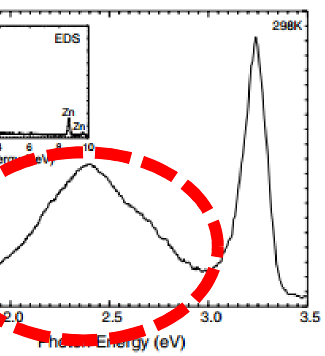
Direct recombination of excitor
through exciton-exciton collision

a et al., "A Comparison of ZnO Nanowires and Nanorods Grown Using MOCVD and Hydrothermal Processes", *J. Electron. Mater.,* Vol. 42,
y 1, 2013.

Traps/Defects in the Visible Spectrum

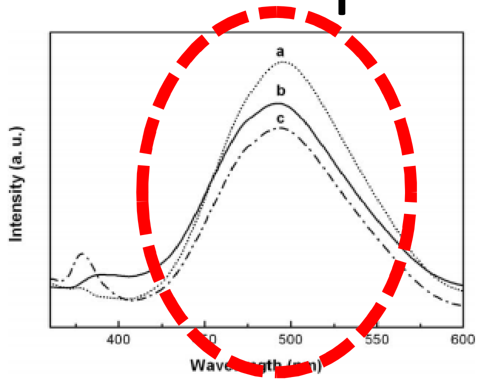
Of... er Growth Techniques

A.J. Djurisic et al. Quantum Electronics Volume 34, Issue 4, Jul... 191–259



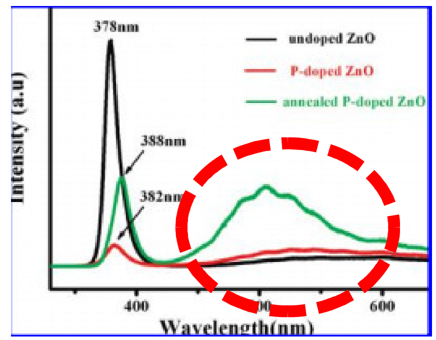
...a Mater., Vol. 52, (2004) 3949-3957

...s grown on GaAs using ... Evaporation



Zeng *et al.* Acta Mater., Vol. 57, (2009) 1813-1820

ZnO NWs grown on TCO using CVD

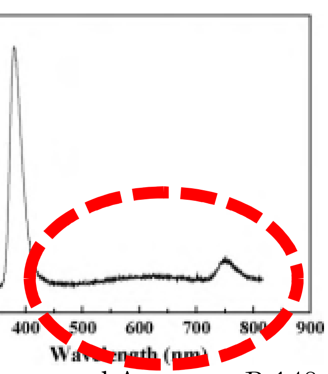


Fang *et al.* J. Phys. Chem. C. Vol 113, No. 50 (2009) 21210

ZnO NWs grown on Si using Hydrothermal Synthesis

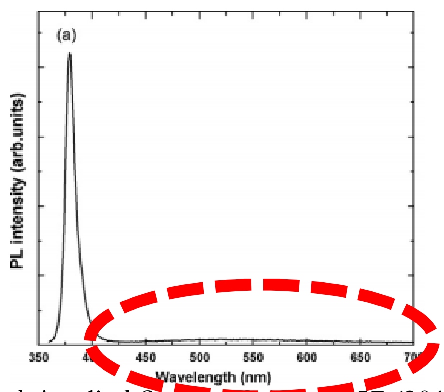
Positions and proposed origin of room temperature PL peaks in ...

Peak position (nm)	Proposed origin
373–390	Near-and-edge emission
~402 (77 K)	O_{Zn}
~446	Shallow donor-oxygen vacancy transi...
~459	Zinc interstitial
~495	Oxygen vacancy
~500/510	Cu^{+}/Cu^{2+}
~510	Surface defects/defect complexes
~510	Singly ionized oxygen vacancy
~520	Zinc vacancy
~520	O_{Zn}
~520	Oxygen vacancies and zinc interstitial...
~540	V_o^{**}
~560	Surface defects
~566 (10 K)	Shallow donor–deep acceptor (zinc va...
~580	Oxygen interstitials, Li impurities
~590	Hydroxyl groups
~626	Oxygen interstitials
~750	Oxygen-related defects, zinc interstitia...



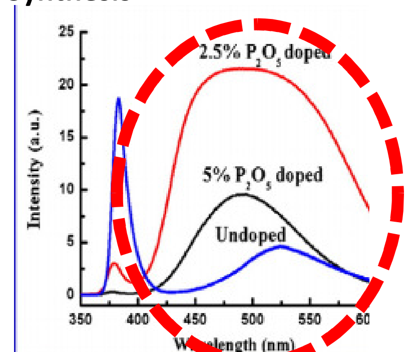
...nsor and Actuators B 148 (2010)

...own on Sapp. Via catalyzed



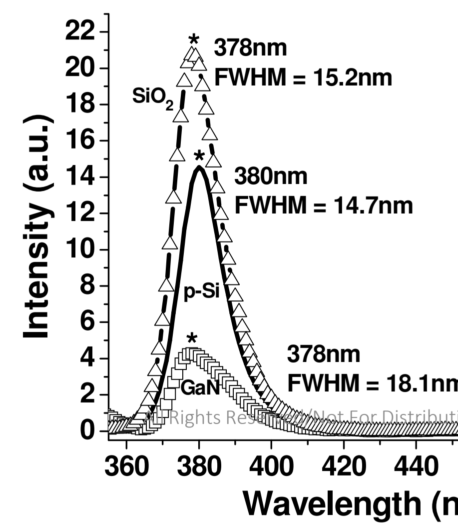
Suh *et al.* Applied Surface Science 257 (2010) 1454-1456

ZnO NWs grown on Si using CVD



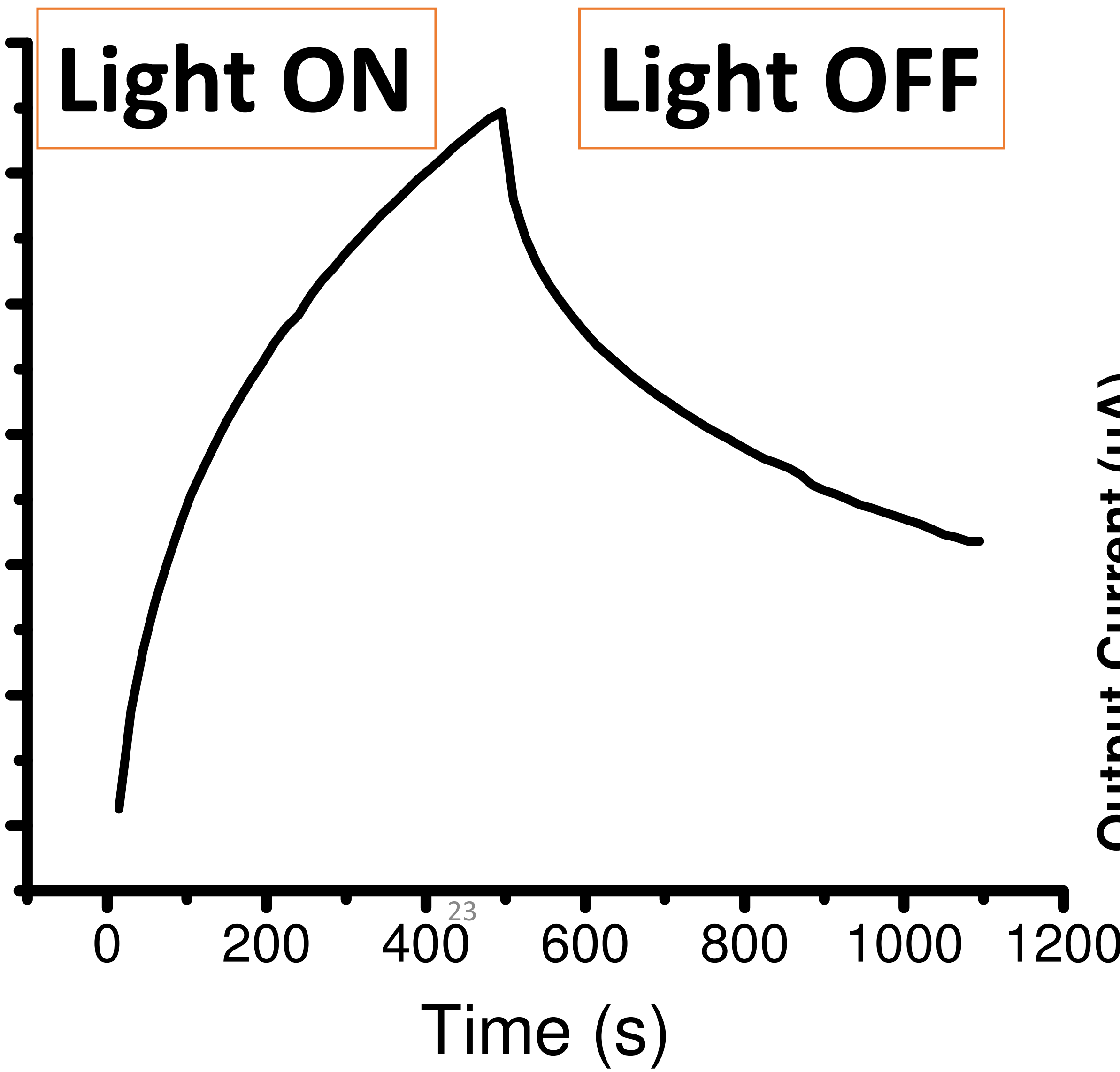
Liu *et al.* Material. Letter., Vol. 70, (2012) 80-82

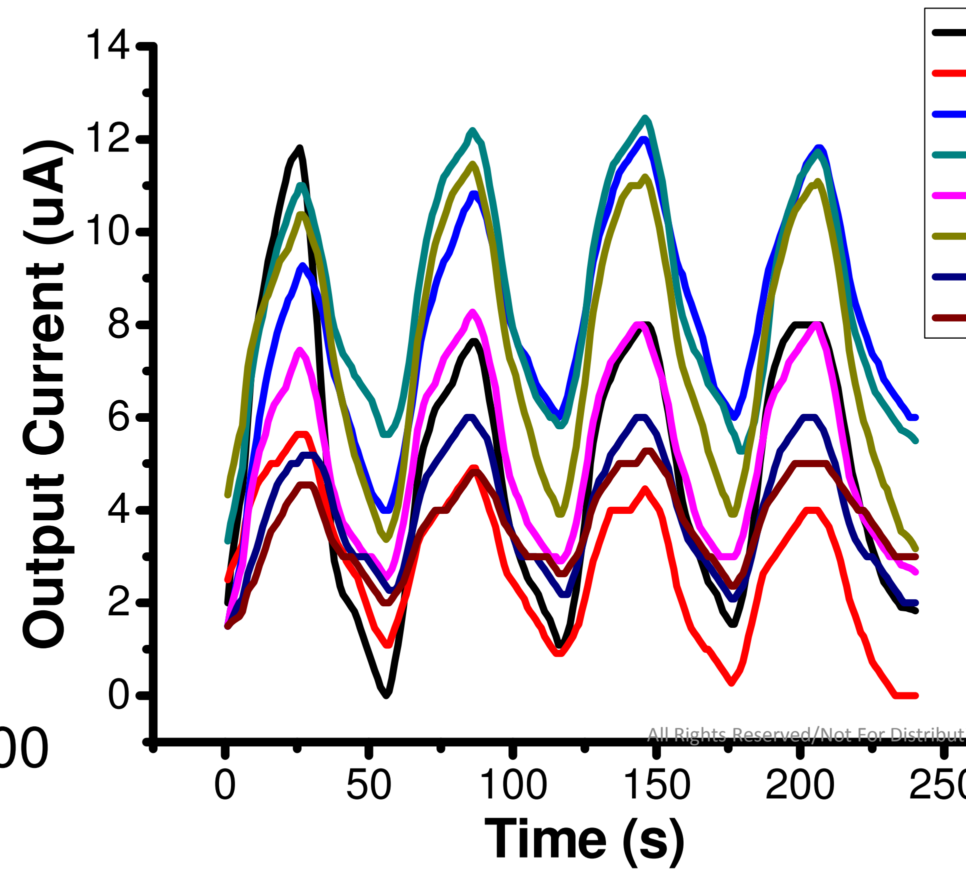
ZnO NWs grown on Sapp using Au film using CVTC



UV of ZnMgO NWs Based Sensor

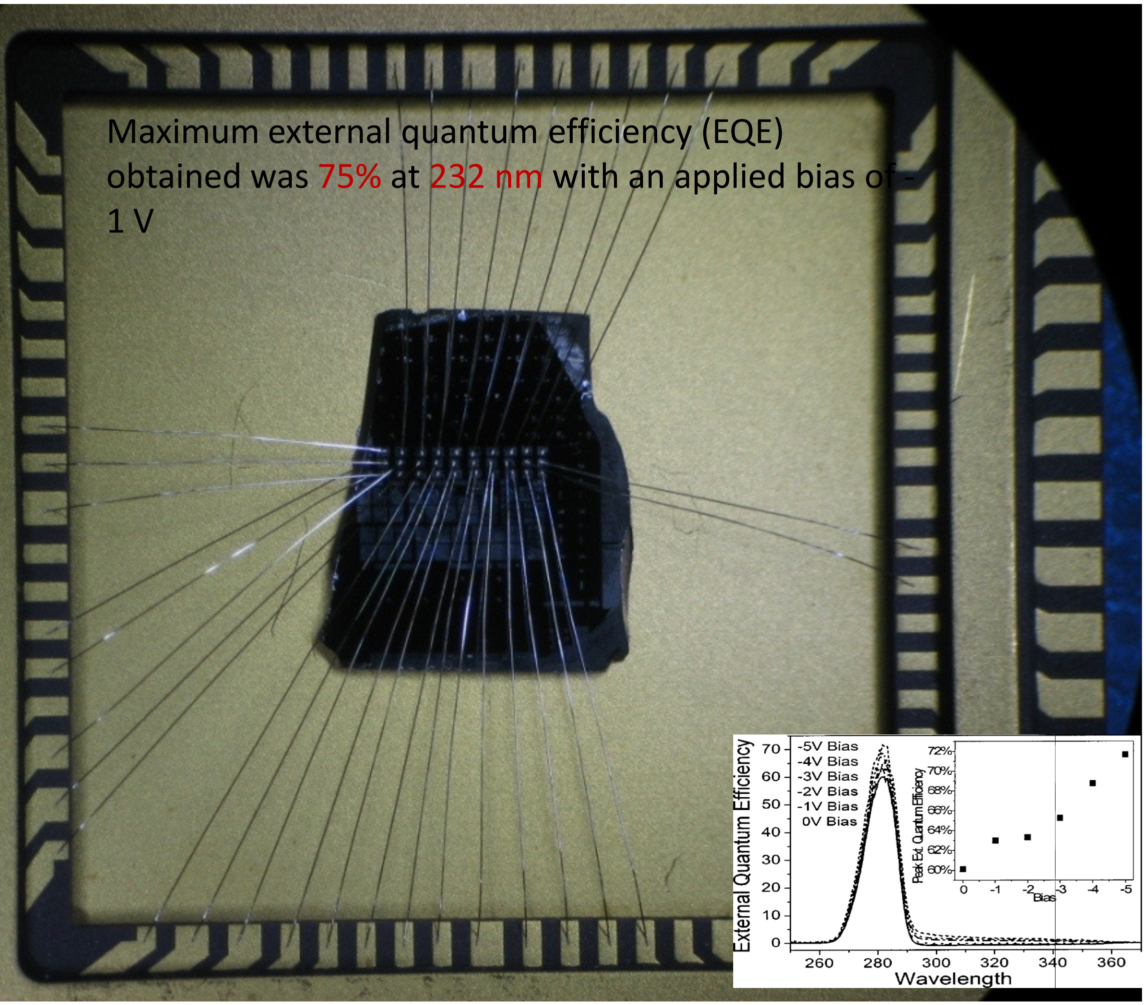
UV Light 355nm with 3V DC Bias



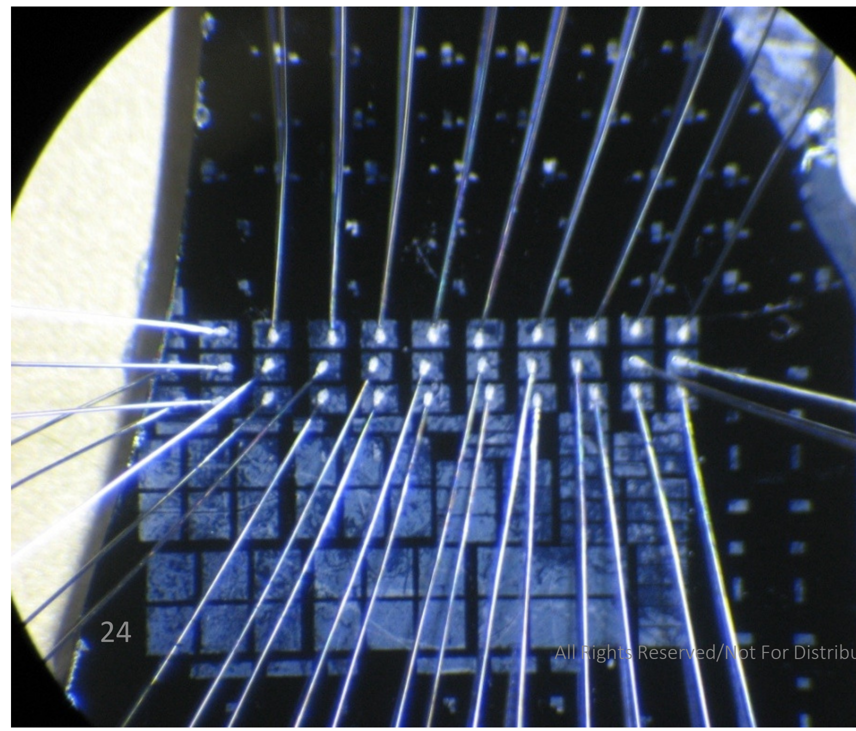


Bonded 9x3 Array of ZnMgO NW-Based Solar Blind Detector

Maximum external quantum efficiency (EQE) obtained was 75% at 232 nm with an applied bias of -1 V

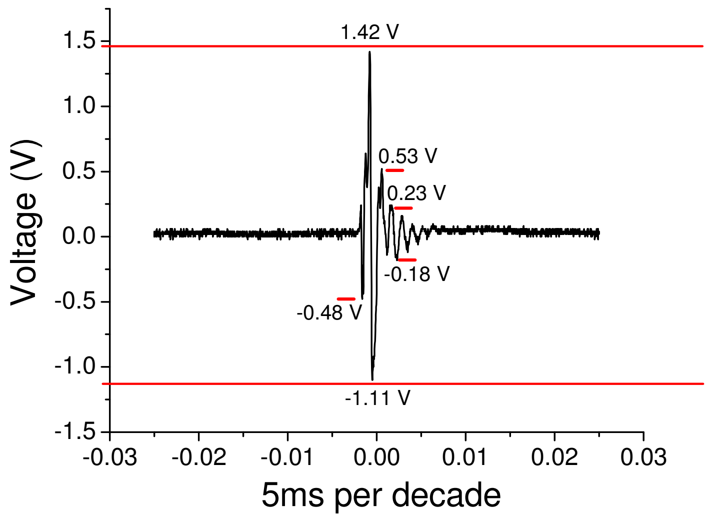


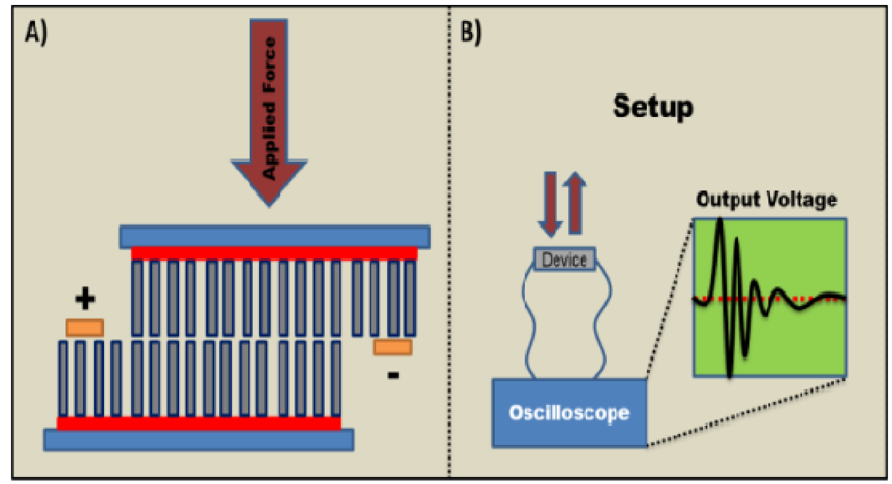
The 9x3 array of solar blind detectors provides **resolution upto 1^0** in the deep uv range (200-300 nm)

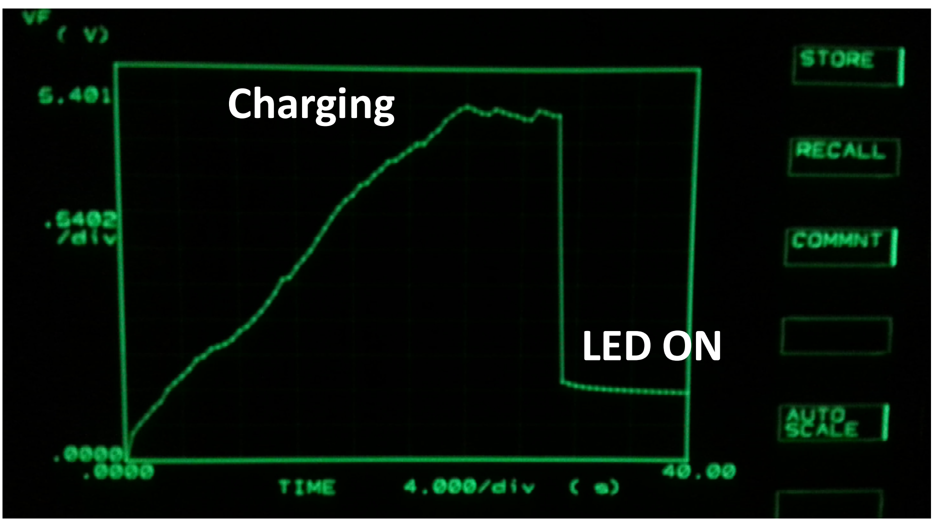


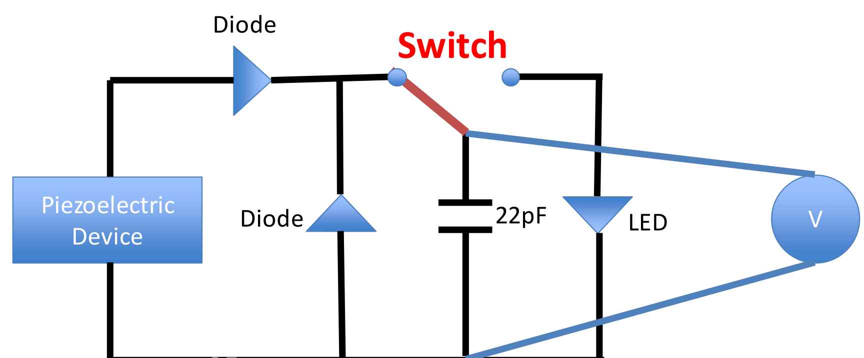
y et al.,"$Zn_{1-x}Mg_xO$-based Deep-Ultraviolet Solar Blind DetectoZn$_{1-x}$Mg$_x$O-based Deep-Ultraviolet Solar Blind Detector" to be submitted AC

Application – Energy Harvesting



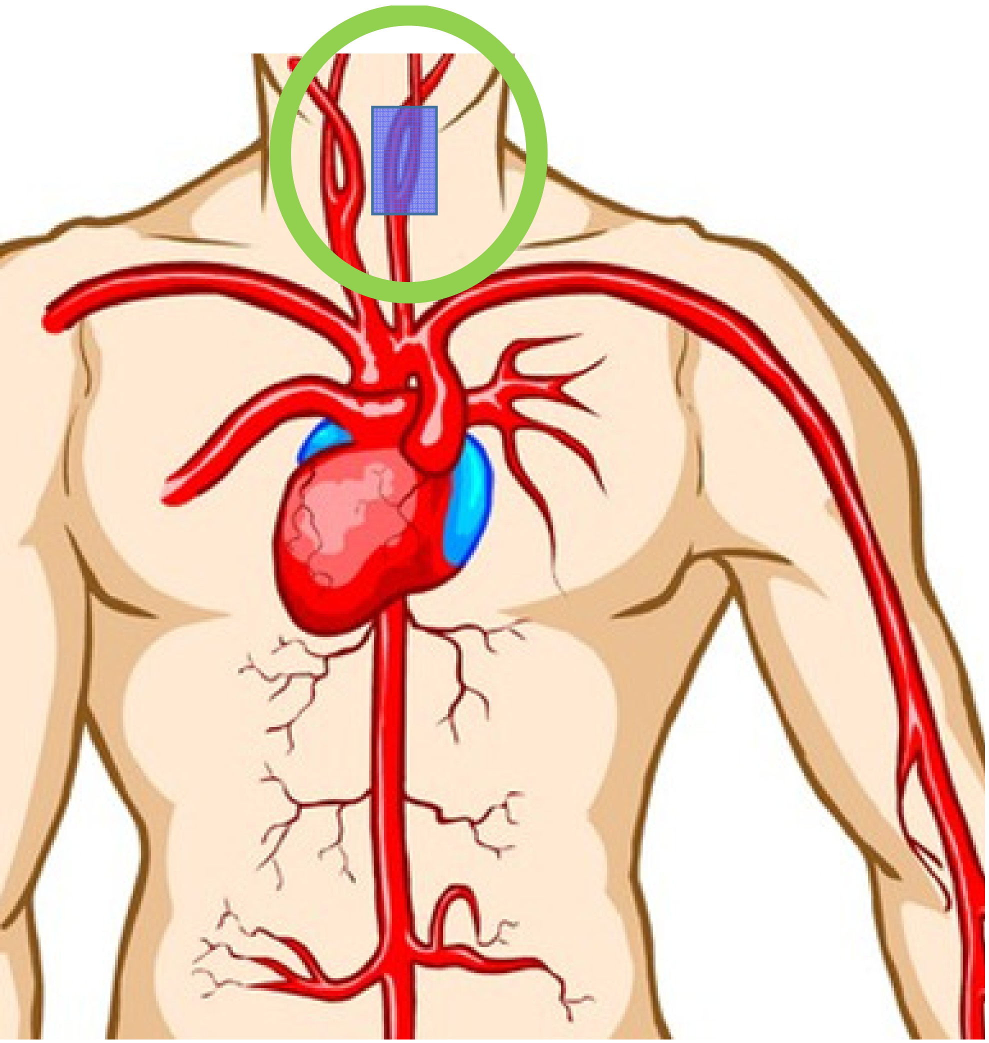




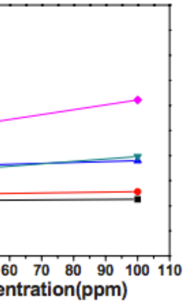


a et al., "Energy scavenging using ZnO nanorods grown on flexible substrates," Lester Eastman Conference on High Performance Devices (L
,4, 7-9 Aug. 2012, doi: 10.1109/lec.2012.6410973

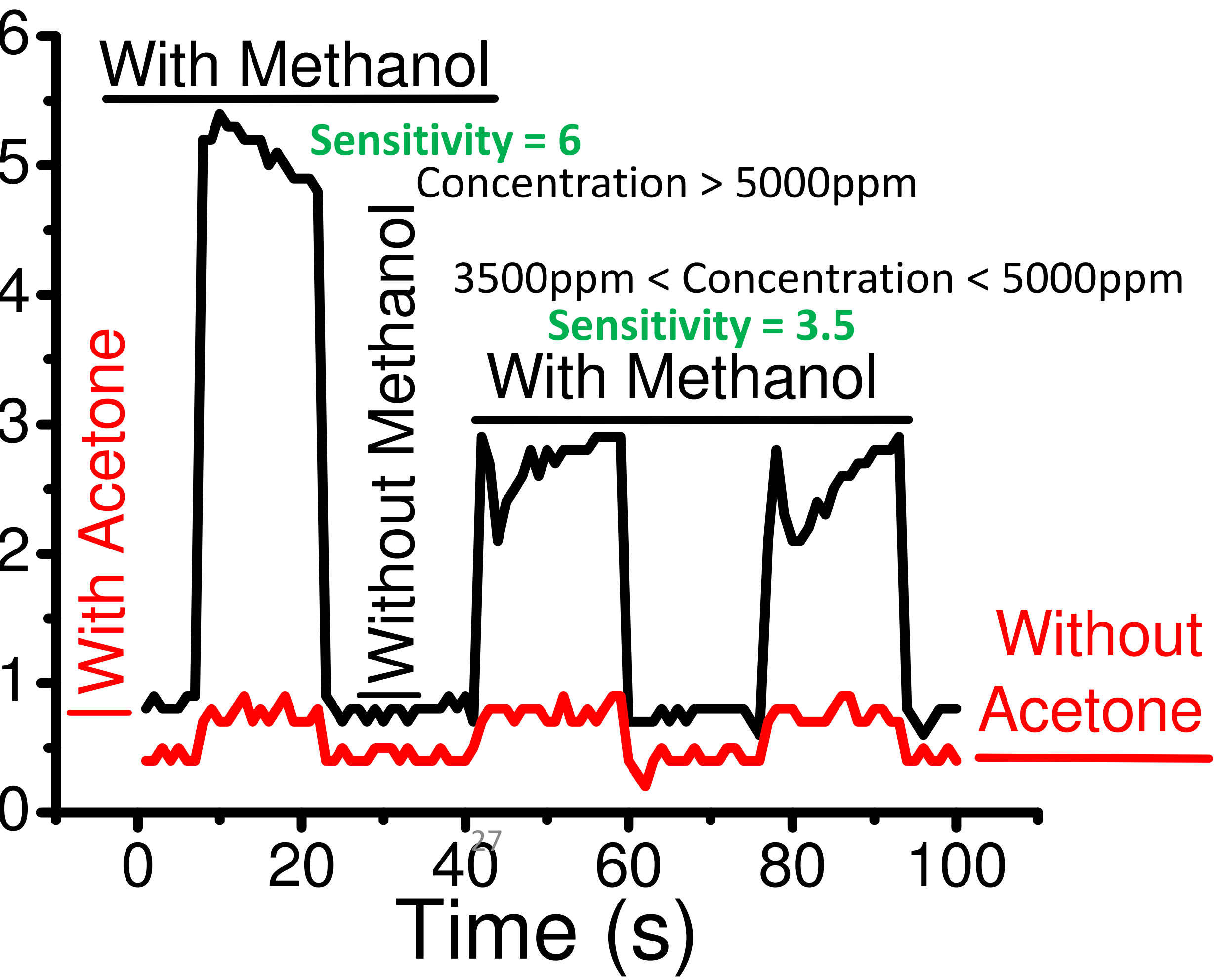
Application – Pulse Monitoring

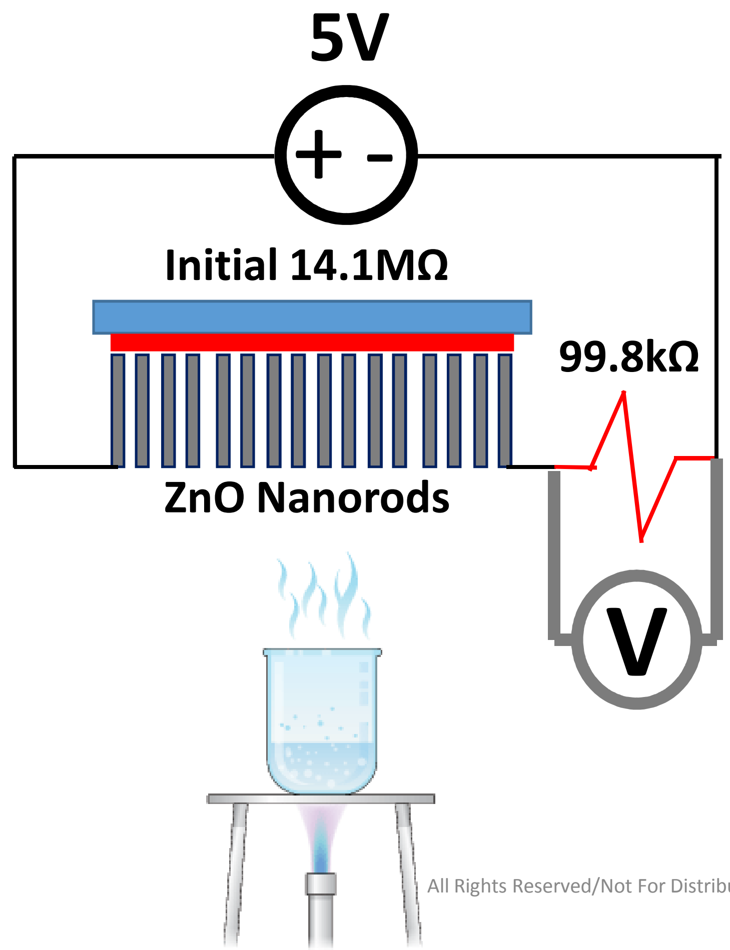


ZnO NRs on Flex. Substrate Gas Sensor



rochemical and Solid-
) (2010) J125





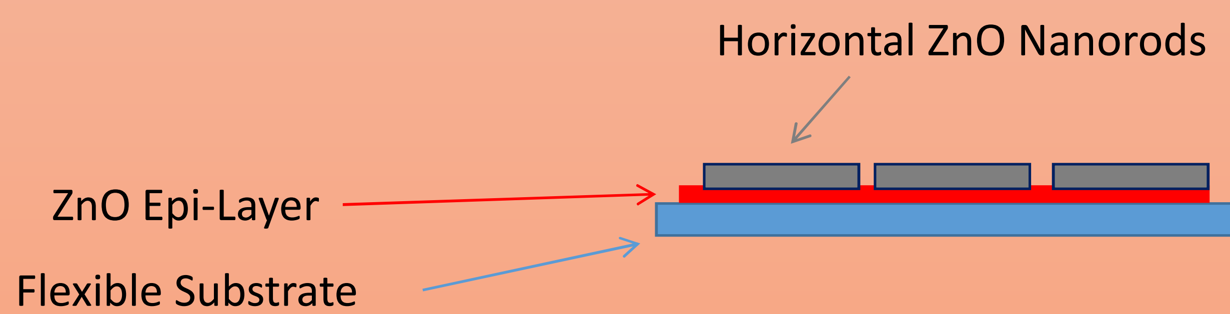
ZnO Horizontal Nanowires

2 Step Epi-Layer

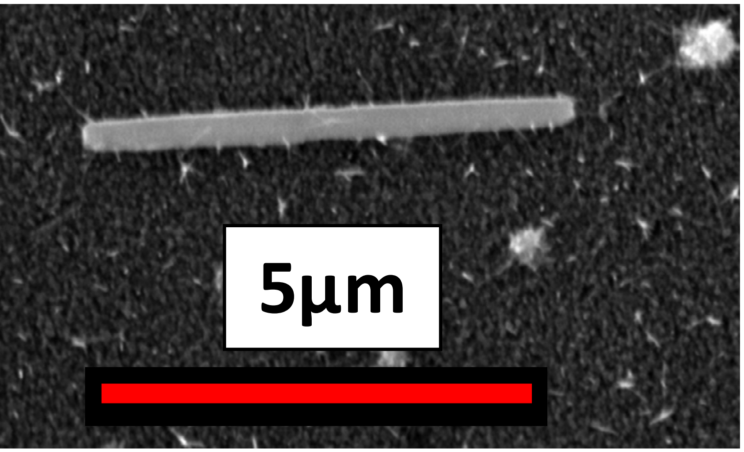
Solution:	Spin	Suspend sample in:
50mL Methanol	500 rpm, 5 sec	0.1M $Zn(NO_3)_2$
0.09g $Zn(CH_3COOH)_2$	3000 rpm, 30 sec	0.1M HMTA
0.12g KOH	10min at 60˚C	60min at 90˚C

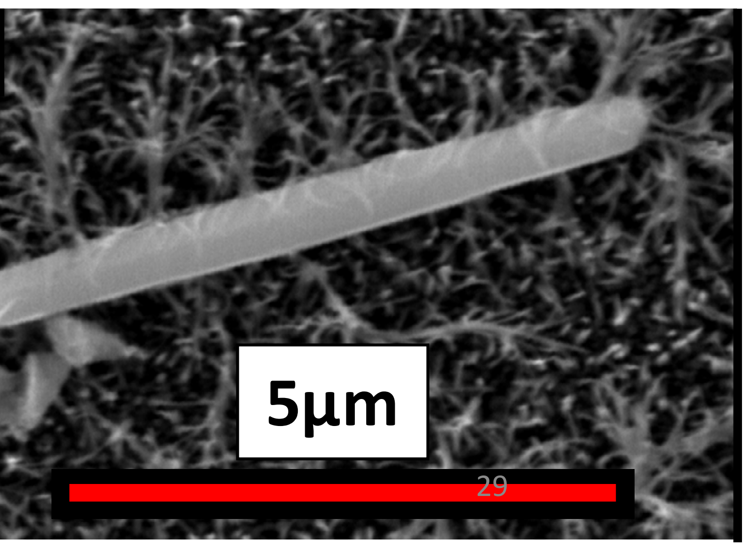
Hydrothermal

Suspend sample in:
5mM $Zn(NO_3)_2$
25mM HMTA
18h at 90˚C



nO Horizontal Nanowires





Diameter: 200 – 500nm
Lengths: 1 – 7 µm

Depending upon:
-growth time
-Zn/OH ratio

Our Method is:

- Simple
- Fast
- Provides TRULY horizontal NRs

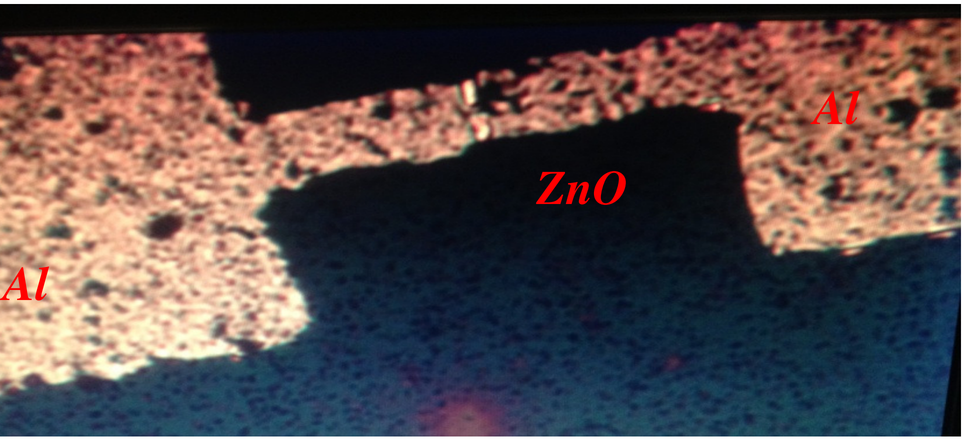
Other Methods Require:

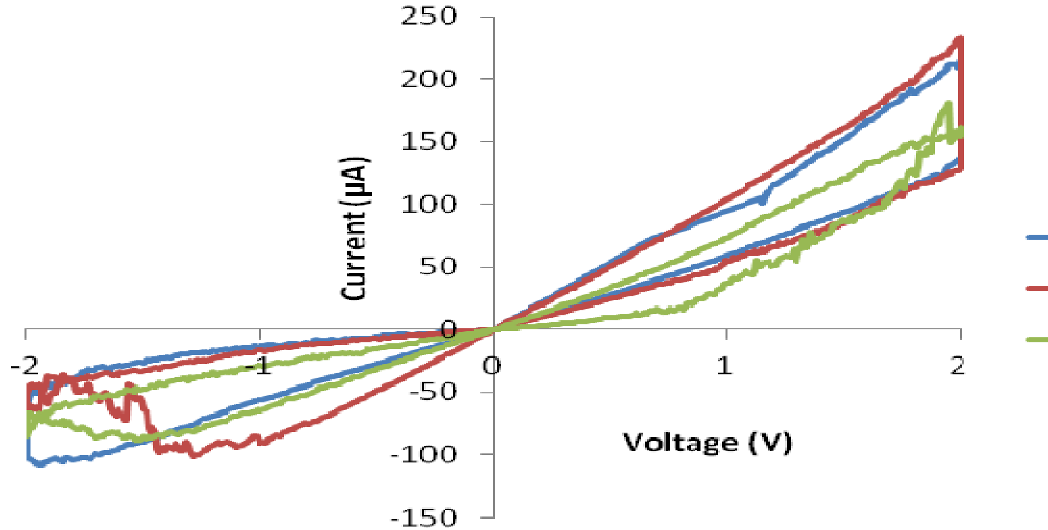
- Pre-treatment of surface
- Patterned and etched seed layer
- Layer to inhibit the nucleation of NR
- AND Don't provide HORIZONTAL NR

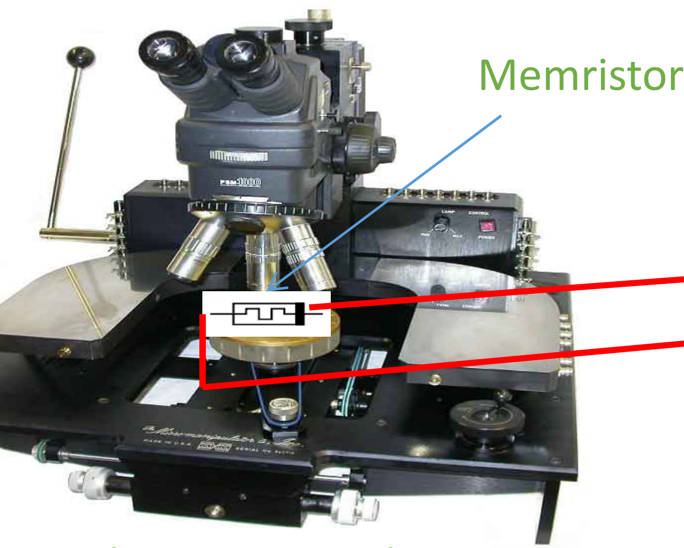
Quasi-Horizontal NI

a et al., "Low Temperature Horizontal ZnO Nanorods", *Materials Research Society (MRS) Spring Meeting & Exhibit,* San Francisco, CA, Ap
be published on MRS Proceedings

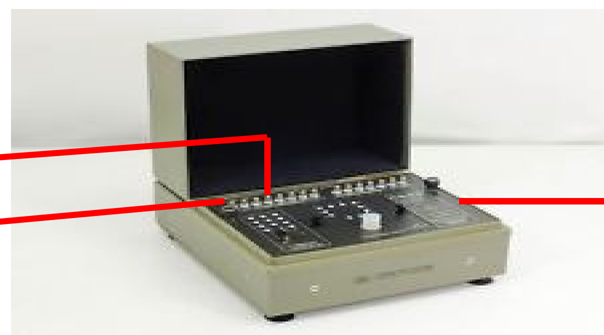
ZnO Memristor







anipulator 6200 Probe Station



16058A Test Fixture

HP4145B Parameter Analyzer

y et al., "Bipolar Resistive Switching Transients in ZnO Nanowire Memristors" submitted to: Electron Device Letter

Mg-Incorporation in $Zn_{1-x}Mg_xO$ via Hydrotherma

gO seed layer spin coated 5 times and aled for 1hr at 150˚C

e NWs was grown at 70C for 7hr using

- 25mM of Zn(NO3)2
- 25mM of HMTA

e NWs was grown at 70C for 7hr using

- 25mM of Zn(NO3)2
- 25mM of HMTA
- 100mM of Mg

tion: ZnO-MgO
w Solubility

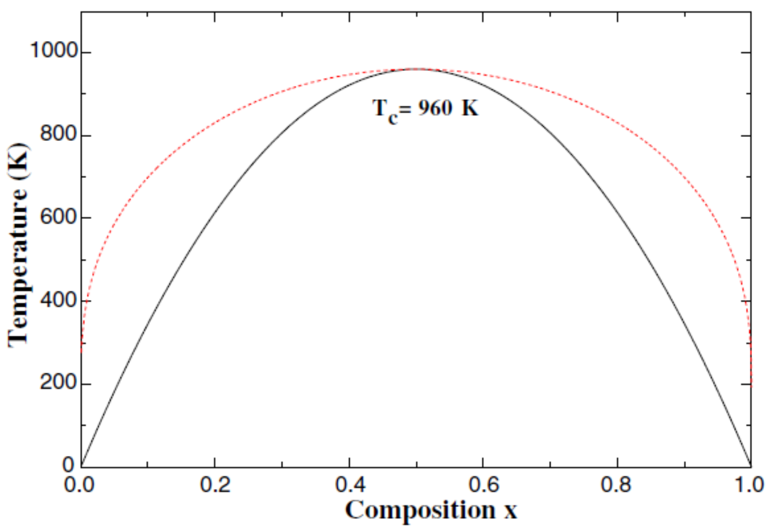
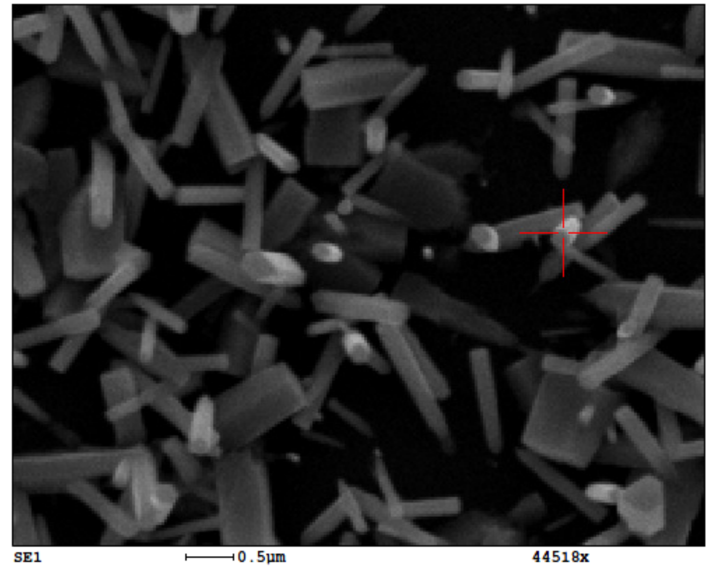
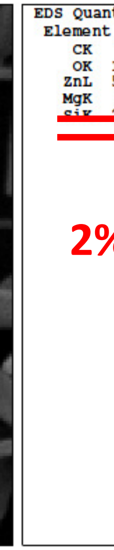


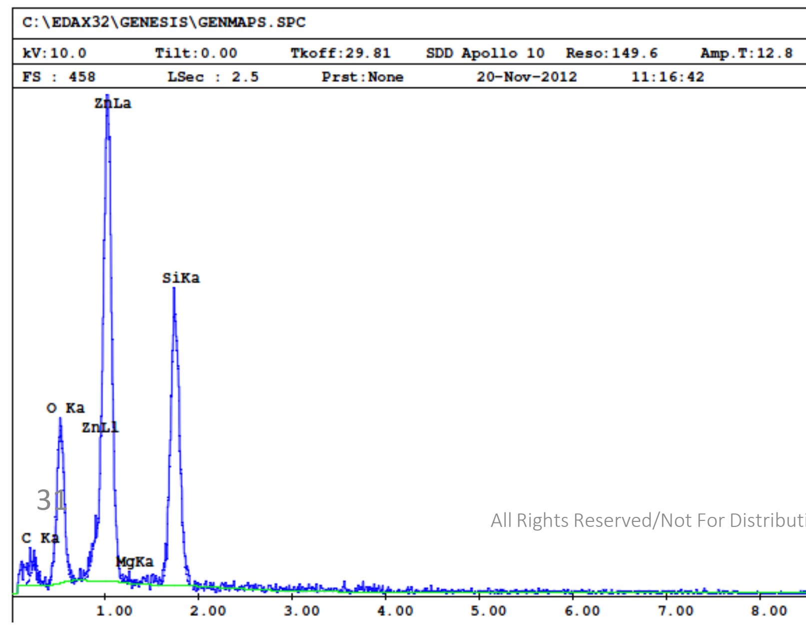
Fig. 9. T–x phase diagram of $Mg_xZn_{1-x}O$ ternary alloy. Solid line: binodal curve; dashed line: spinodal curve.

B. Amrani et al., Computational Materials Science 40 (2007) 66–72



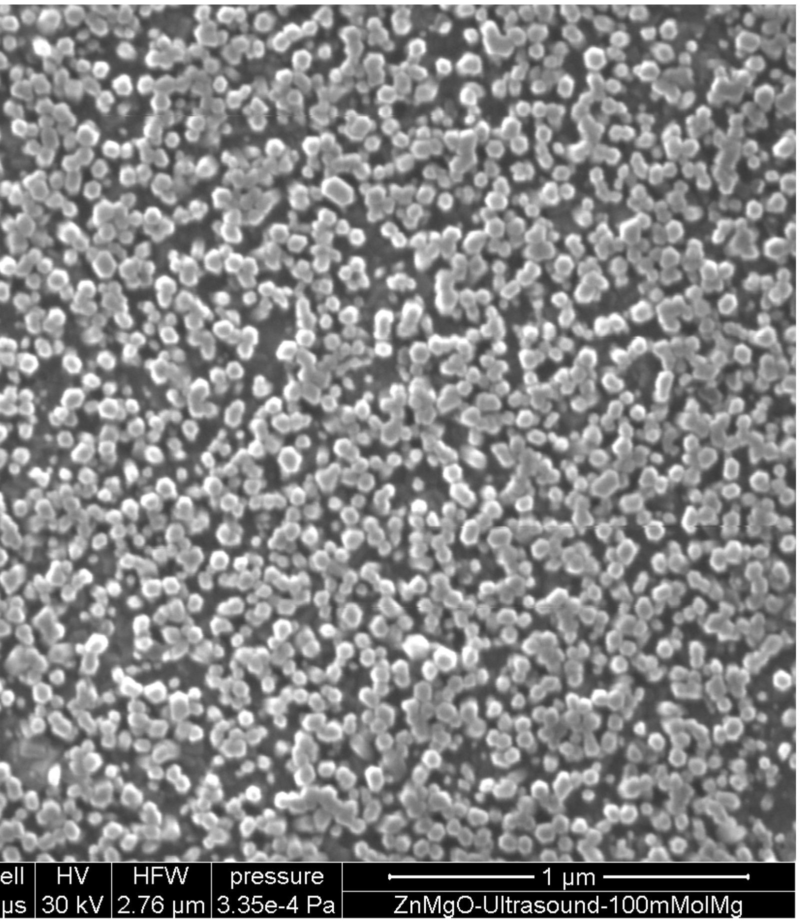


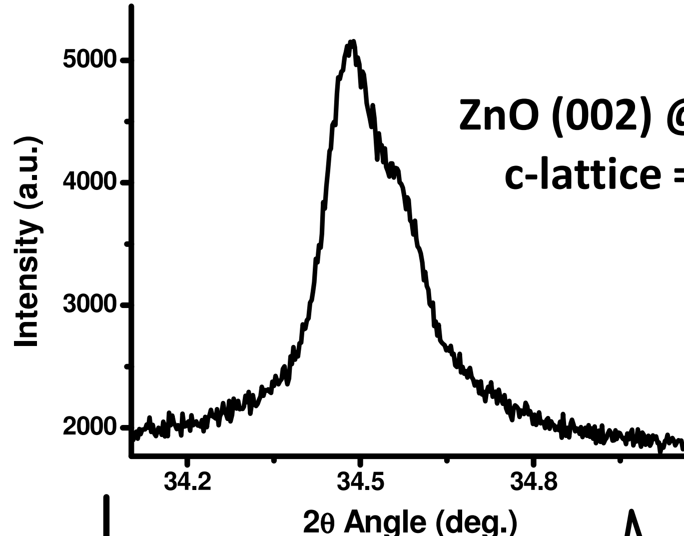
2%

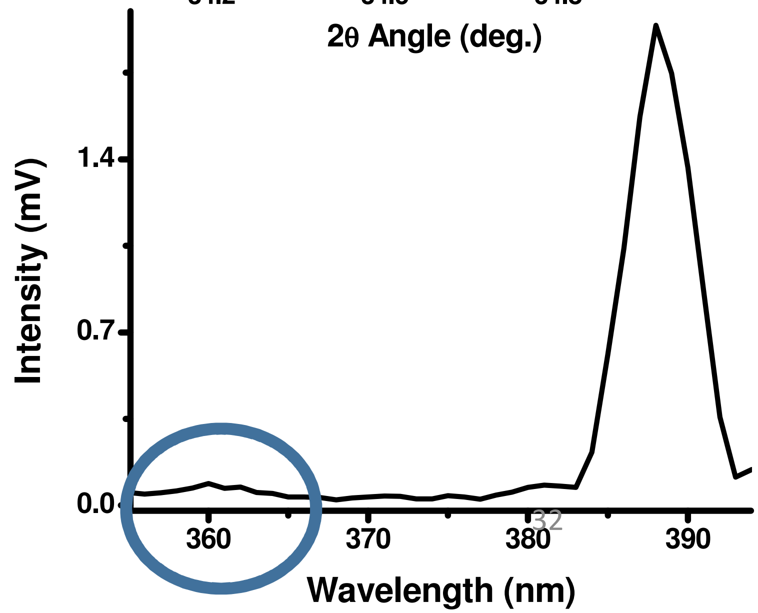


rcoming 4% Mg-Incorporation in $\underline{Zn_{1-x}Mg_xO}$ via ochemical

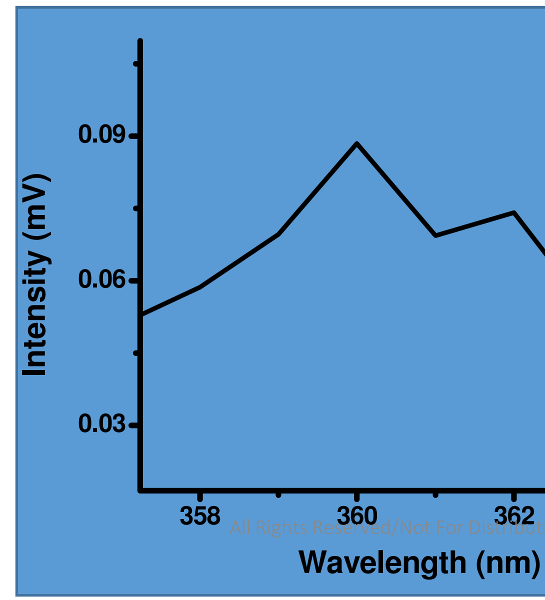
er: 30 – 60 nm **EDS** = 5-7.5% Mg







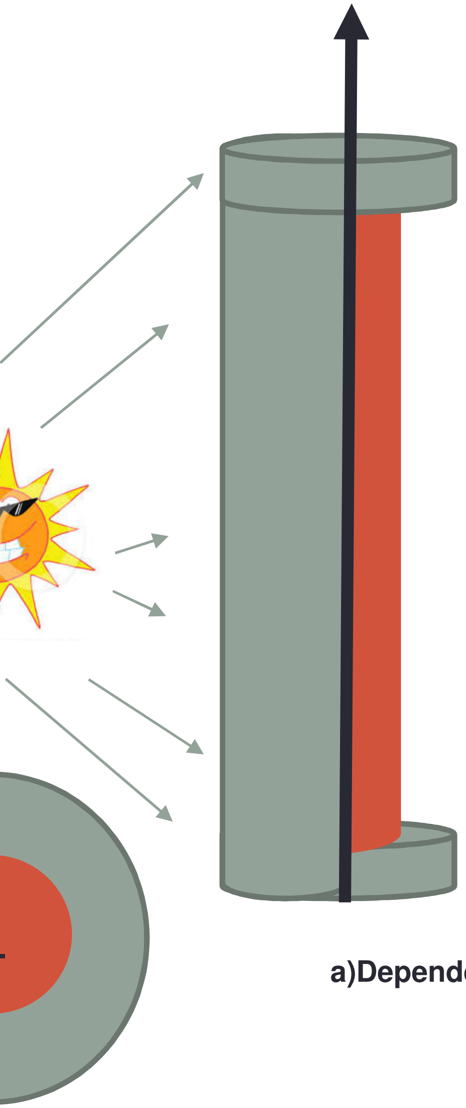
NBE Shifted from 389nm to



a et al., "Overcoming 4% Mg-Incorporation in $\underline{Zn_{1-x}Mg_xO}$ via Sonochemical", *in preparation*

Core-Shell Photovoltaic Applications

is Absorbed along the NW (**axial**)
ection of e⁻ depends **radially**
, **less recombination**
er Absorption Coeff. due to size of



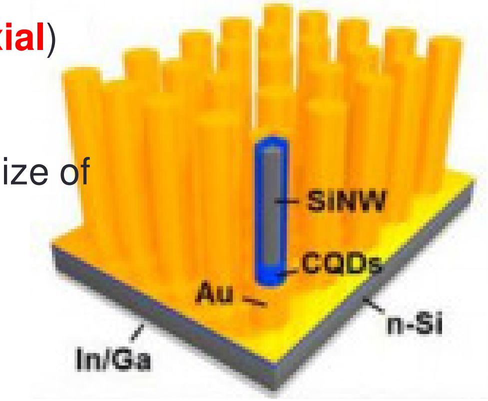
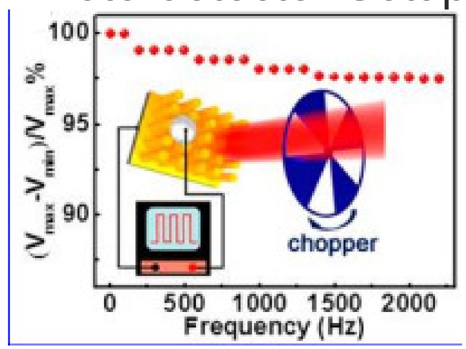
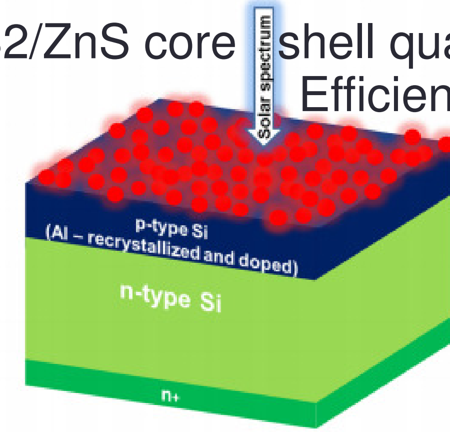
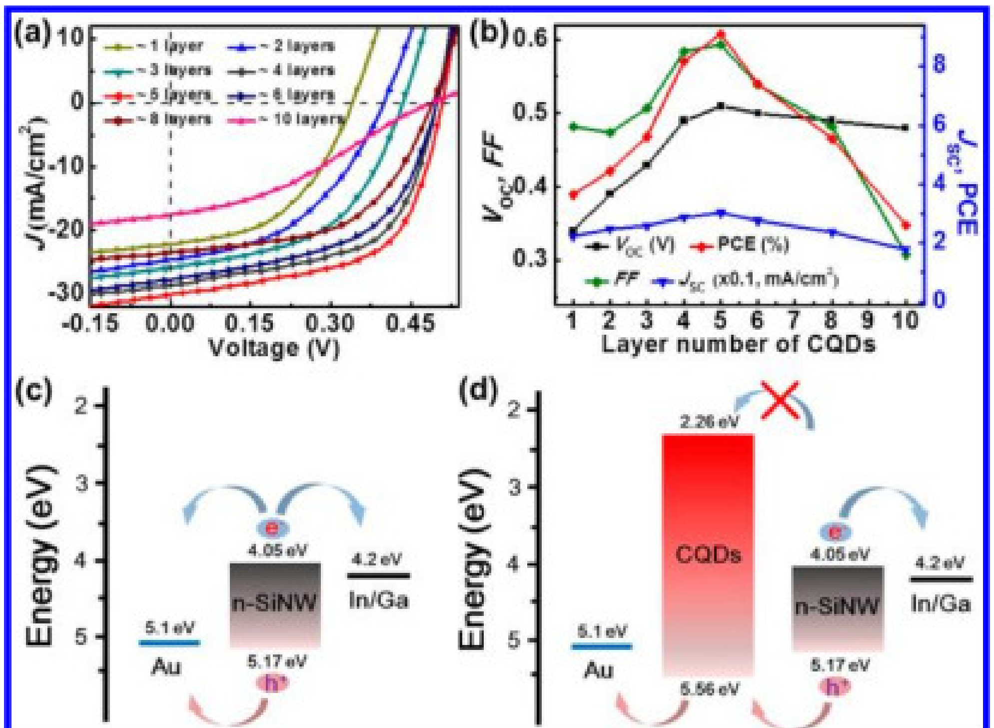


Photo-detector Setup



CuInS2/ZnS core shell quar
Efficienc

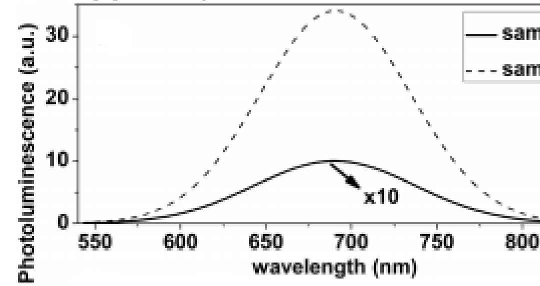




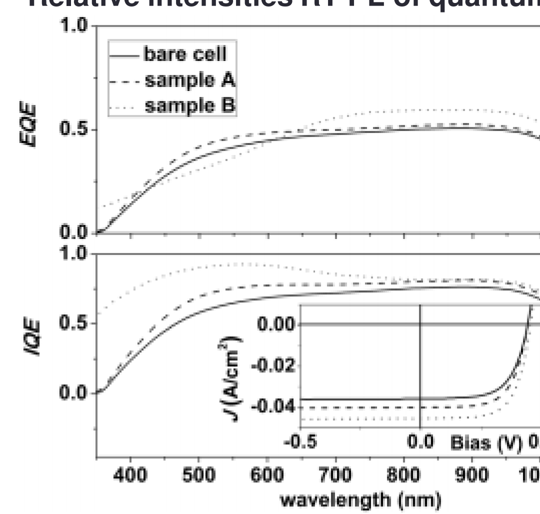
a)Dependence of Photovoltaic Characteristics of SiNW array/CQD heterojunction device
b)Plot of Voc, Jsc, FF and PCE as function of CQD layer number
c)Energy band diagram of Au/SiNW Schottky junction
d)SiNW/CQD heterojunction

ACS Nano 8, 4015-4022 (2014)

Appl. Phys. Lett. 104, 183902 (2



Relative intensities RT PL of quantun



ZnMgO/ZnO Coaxial Core-Shell

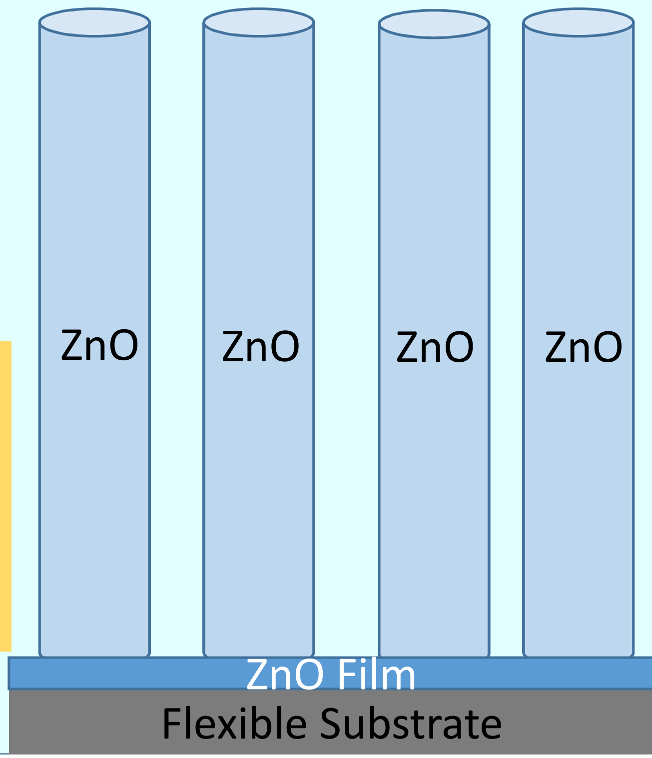
seed layer
L Methanol
g $Zn(CH_3COOH)_2$
g KOH

Growth ZnO NRs:

Spin
500 rpm, 5 sec
3000 rpm, 30 sec
10min at 60˚C

n film using
ermal
d sample in:
$(NO_3)_2$
MTA
t 90˚C

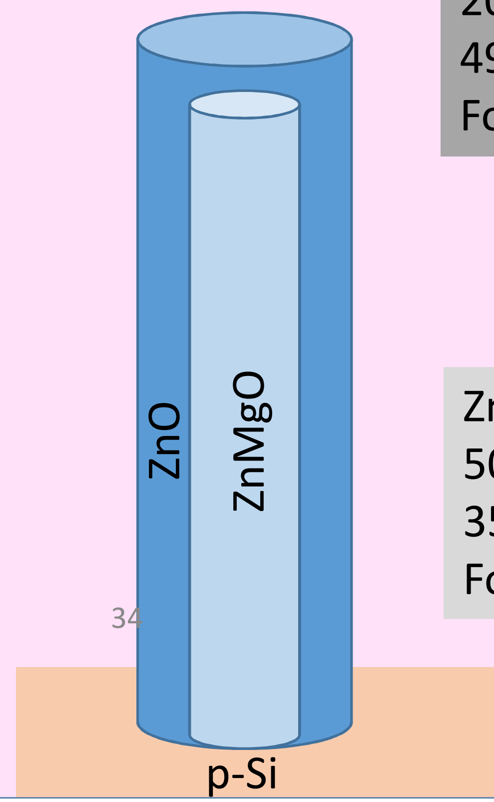
using Hydrothermal:
sample in:
$NO_3)_2$
TA
C



ZnO seed using MOCVD:
50sccm DEZn @ 300Torrs
35sccm N_2O + 0.5slpm N_2
For 20 min, 70 Torr, 300°C

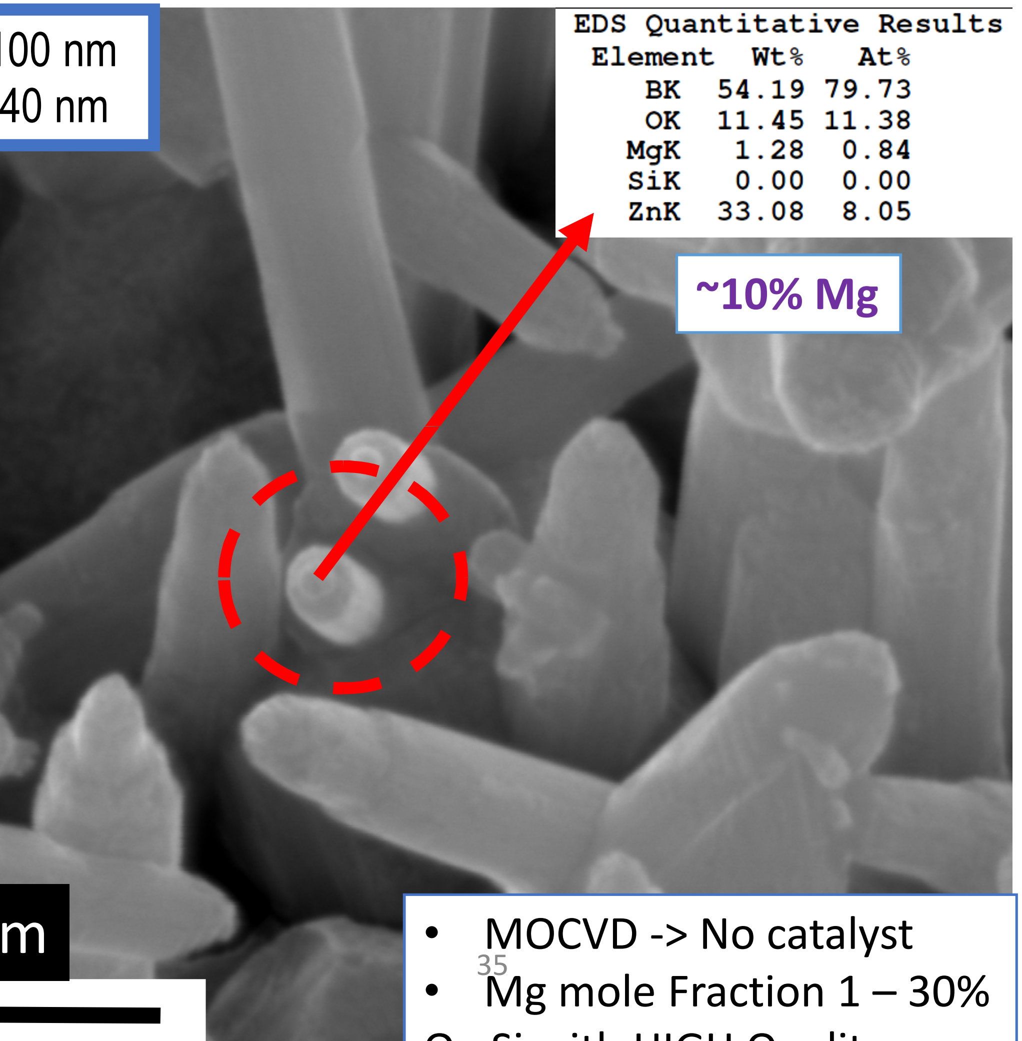
Growth
ZnMgO
Core-Sh

ZnMgO NWs (Shell) us
MOCVD:
10sccm DEZn @ 300To
200sccm Cp2Mg @ 25
499sccm N_2O + 0.5slp
For 15 min, 0.5 Torr, 6



ZnO (Shell)using MOC
50sccm DEZn @ 300To
35sccm N_2O + 0.5slpn
For 20 min, 70 Torr, 30

ZnMgO/ZnO Coaxial Core-Shell



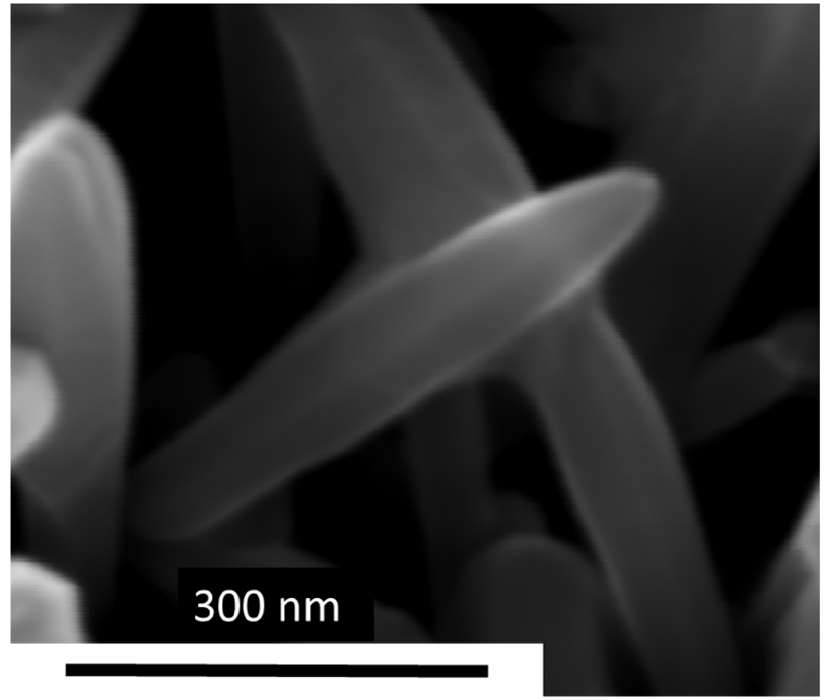
EDS Quantitative Results

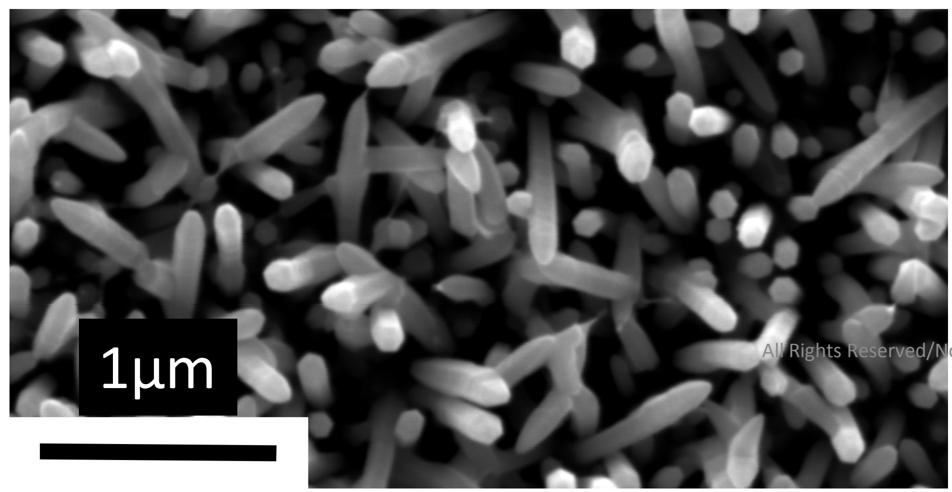
Element	Wt%	At%
BK	54.19	79.73
OK	11.45	11.38
MgK	1.28	0.84
SiK	0.00	0.00
ZnK	33.08	8.05

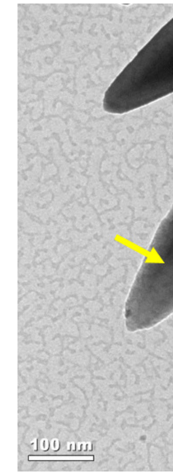
- MOCVD -> No catalyst
- Mg mole Fraction 1 – 30%

On Si with HIGH Quality

- Vertically aligned



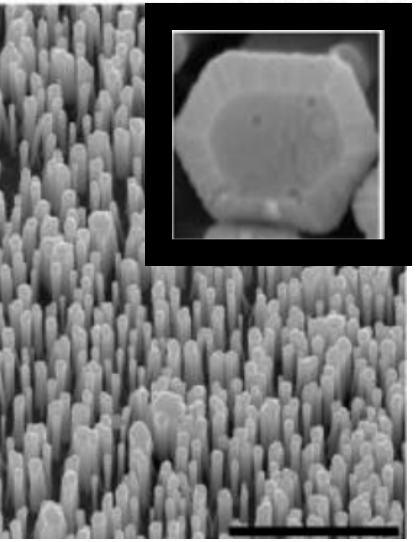




Abdi
al., "F
of Zn
Core-
Struct
and U
Senso
onal
Semic
Devic
Symp
Bethe
Dec 1
and u
Solid
Elect

gO 10 – 25nm
70 – 150nm

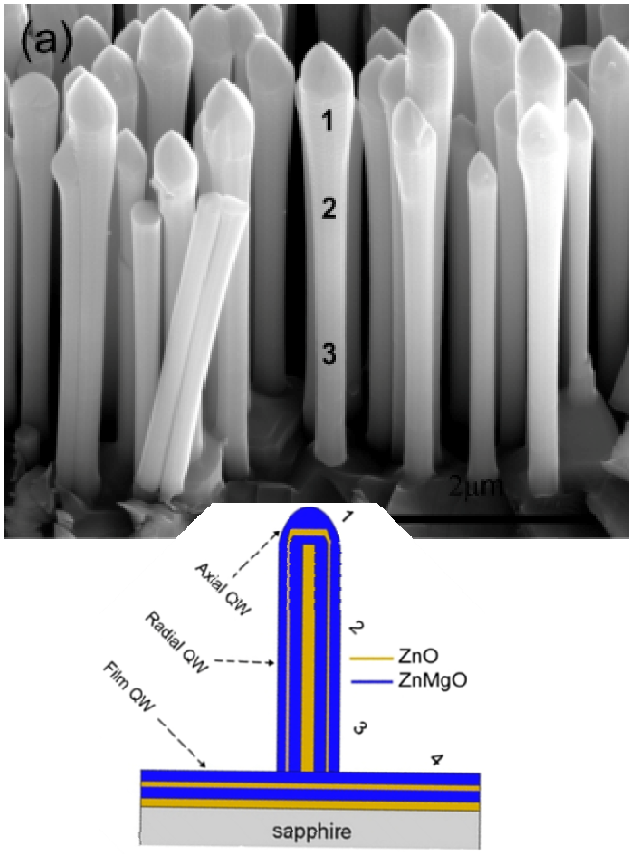
Reported Work



nMgO Core-Shell
sing Hydrothermal
ed Laser Deposition

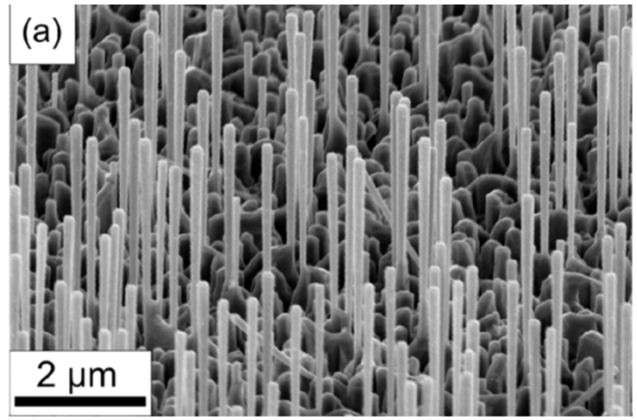
Defects at 450 – 800nm

W. Liu et al J. Phys. Chem. C 114 (2010) 16148



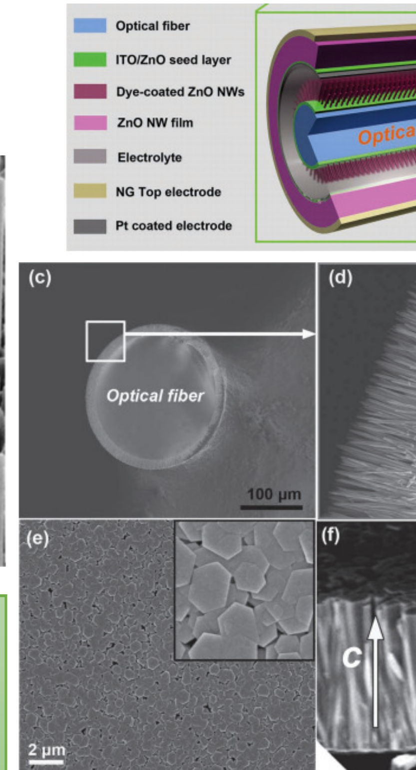
Multiples ZnO/ZnMgO Core-Shell layers grown Using Pulsed Laser Deposition

B.Q. Cao et al Nanotechnology 20 (2009) 305701



Multiples ZnO/ZnMgO Core-Shell layers grown Using Metal Organic Vapor Phase Epitaxy

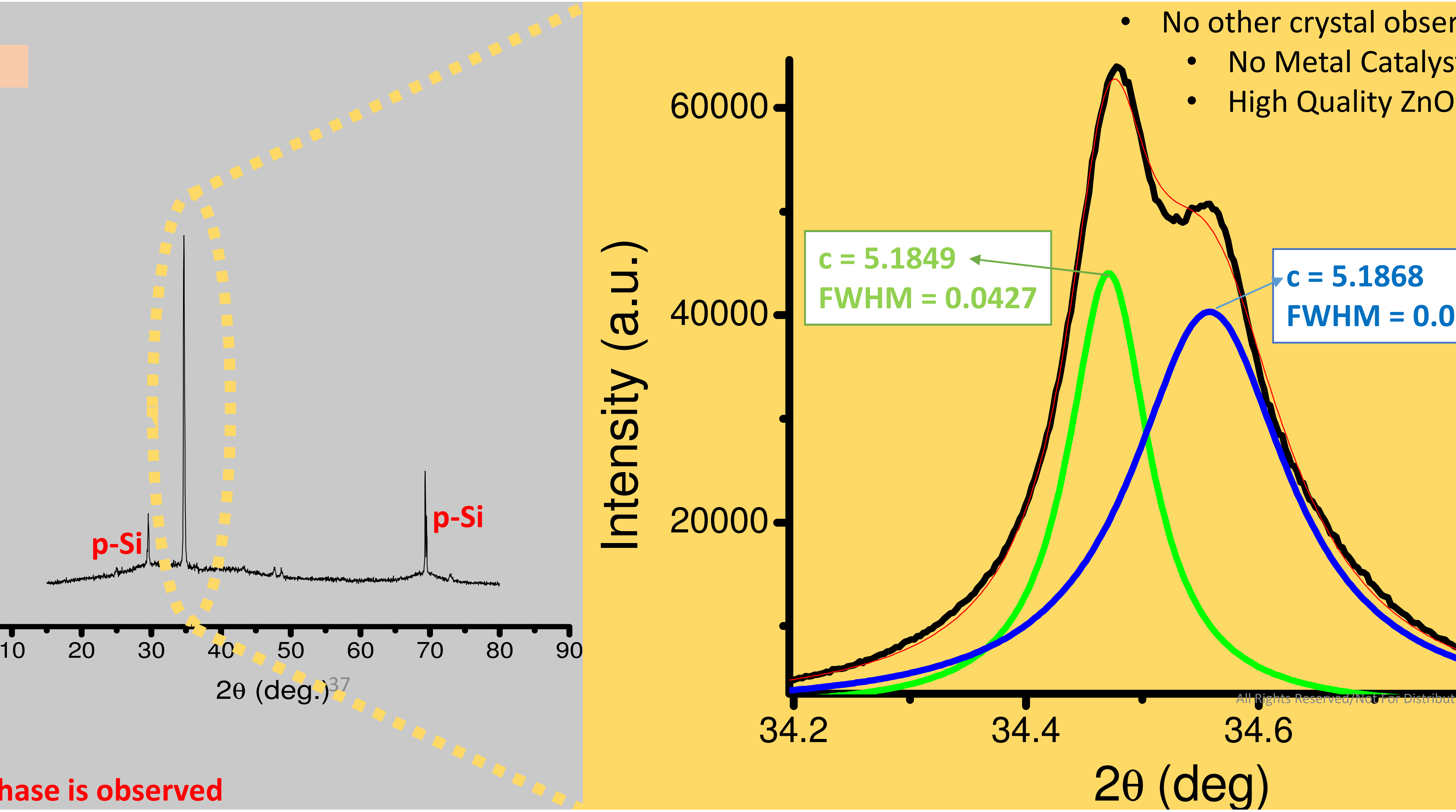
R Thierry et al Nanotechnology 23 (2012) 085707



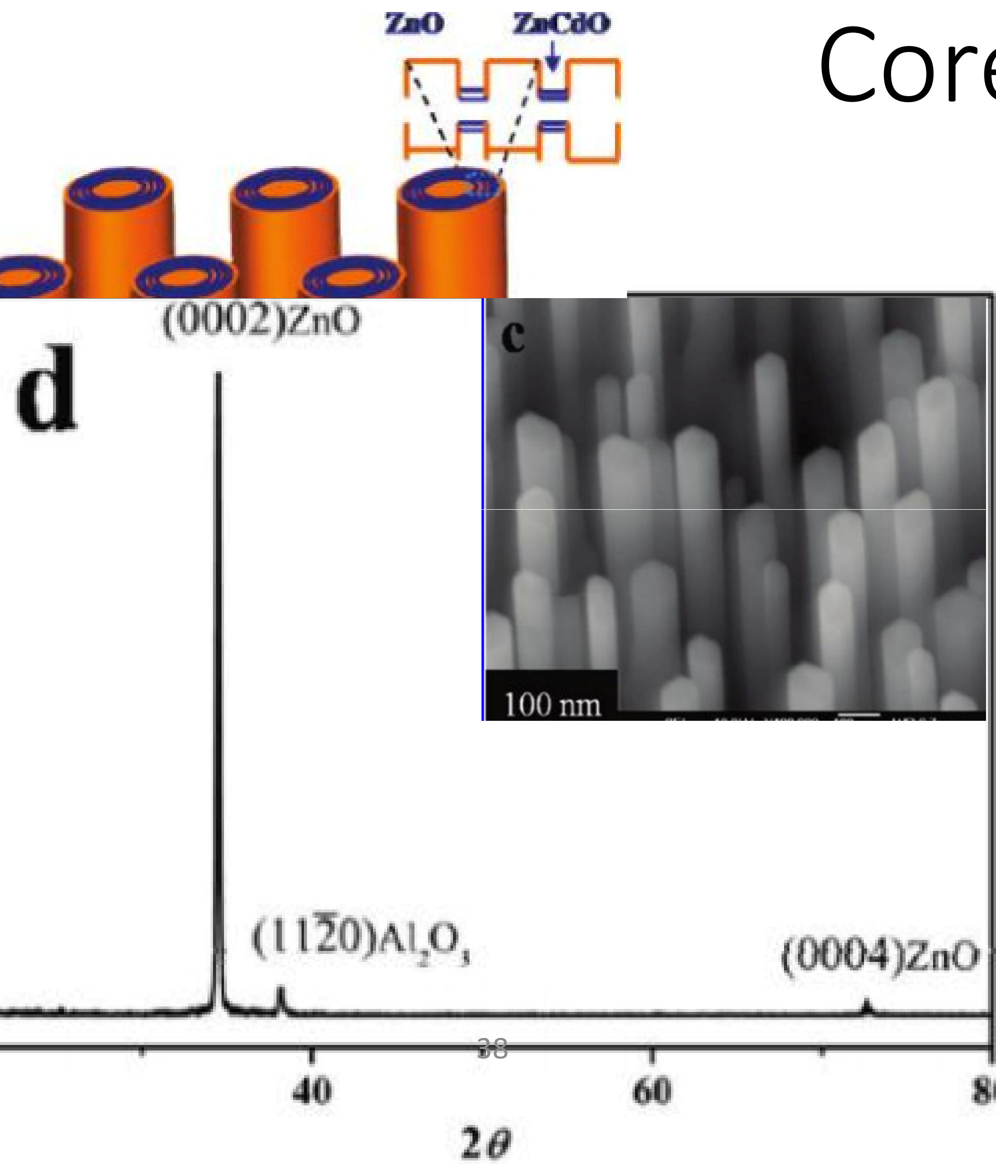
NWs arrays are g
radially around
optical fiber with t
pointing outwa

C. Pan, Adv. Mater. 24 (20

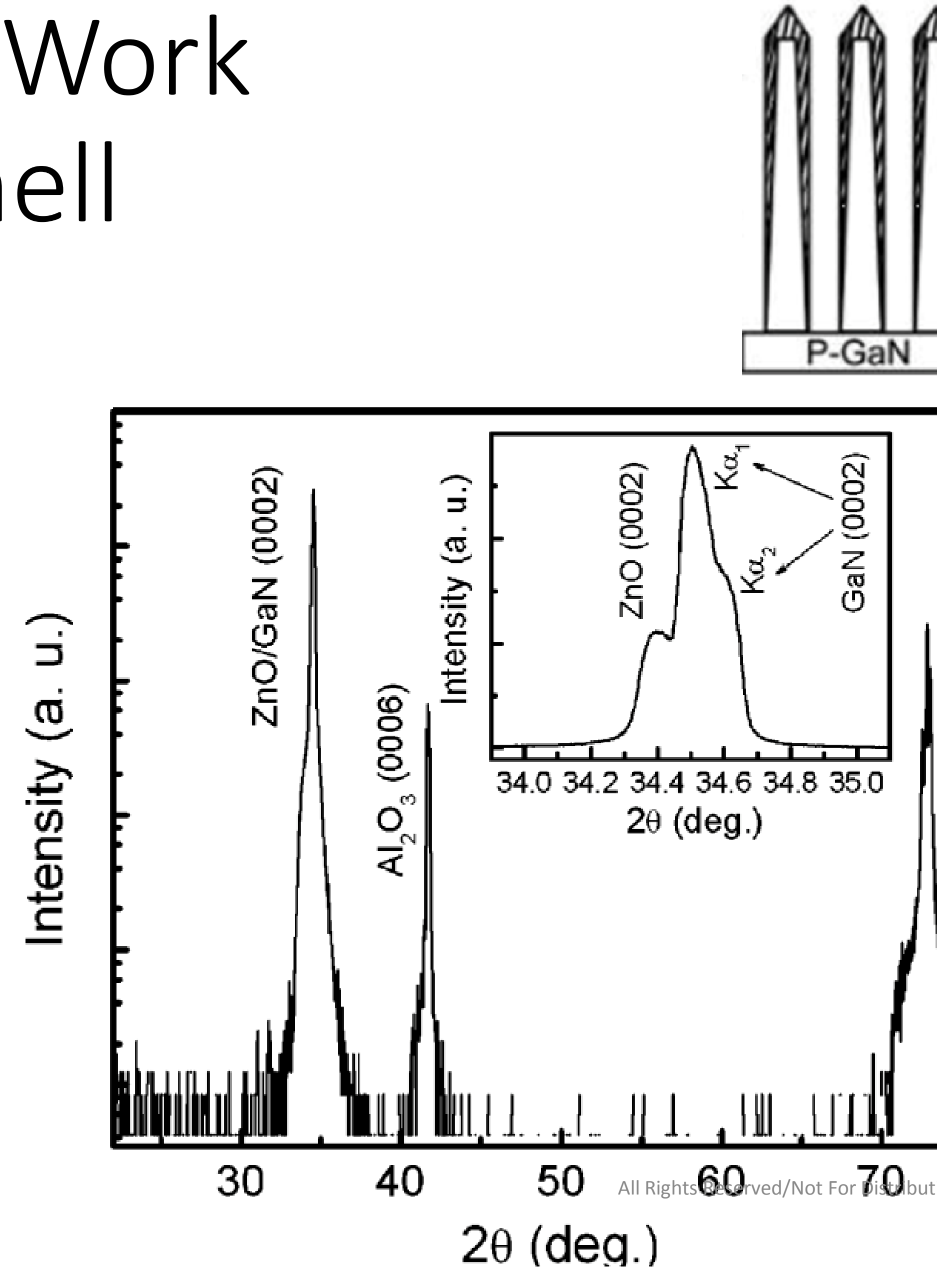
XRD – ZnMgO/ZnO Coaxial Core-Shell



Reported Work
Core-Shell

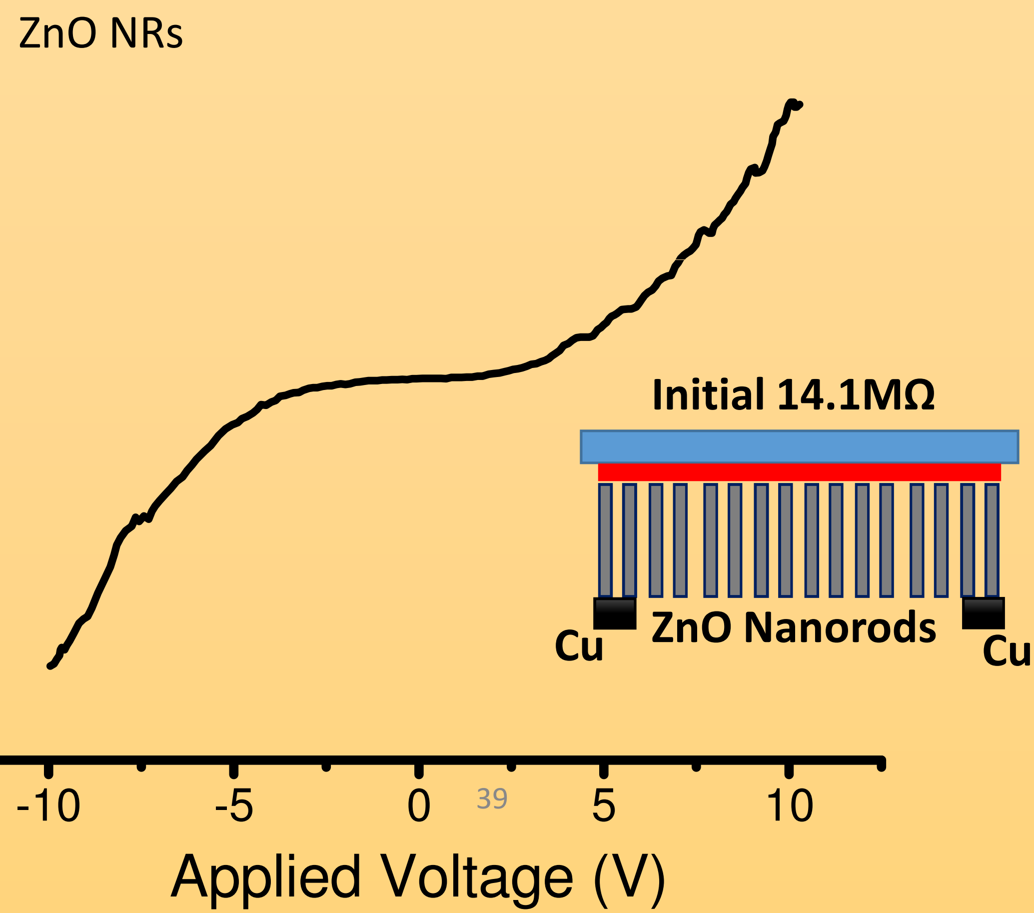


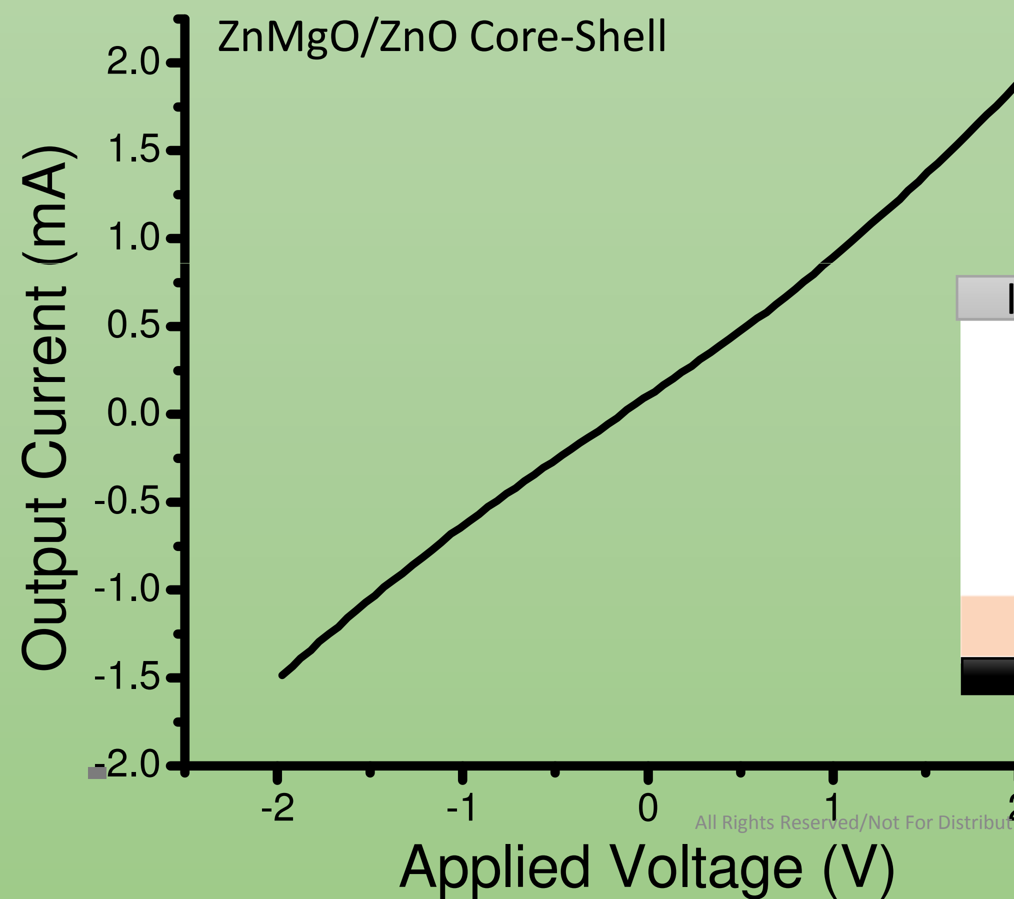
C. Chem et al J. Phys. Chem. C 114 (2010) 3863



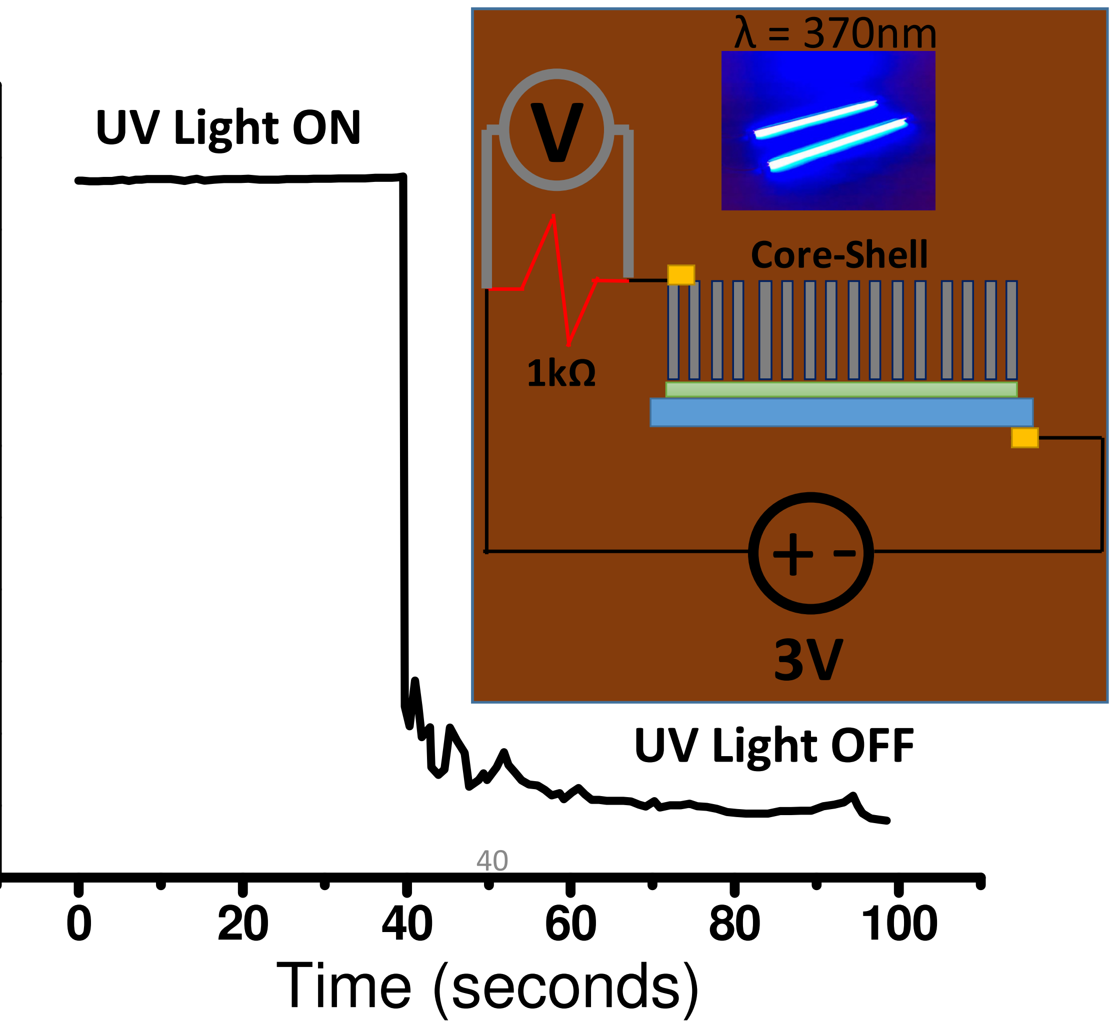
W. Liu et al J. Phys. Chem. C 114 (2010) 16148

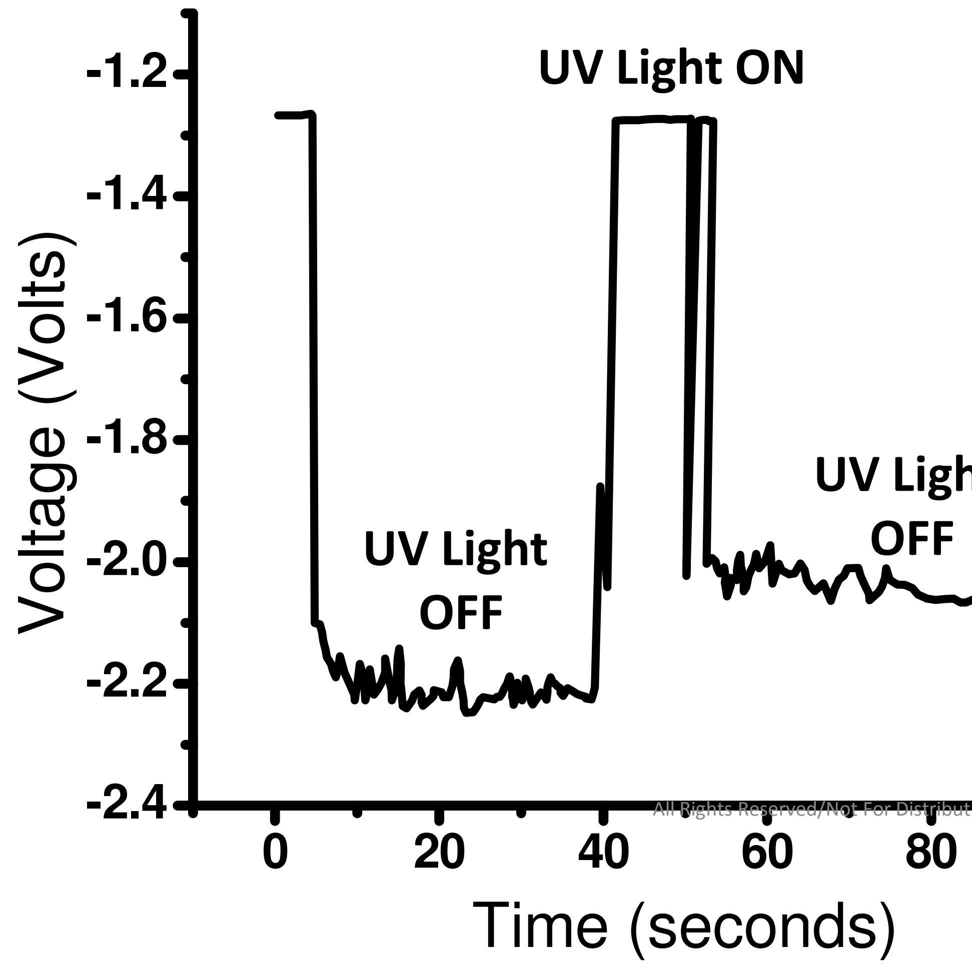
DEVICES I-V Characterization



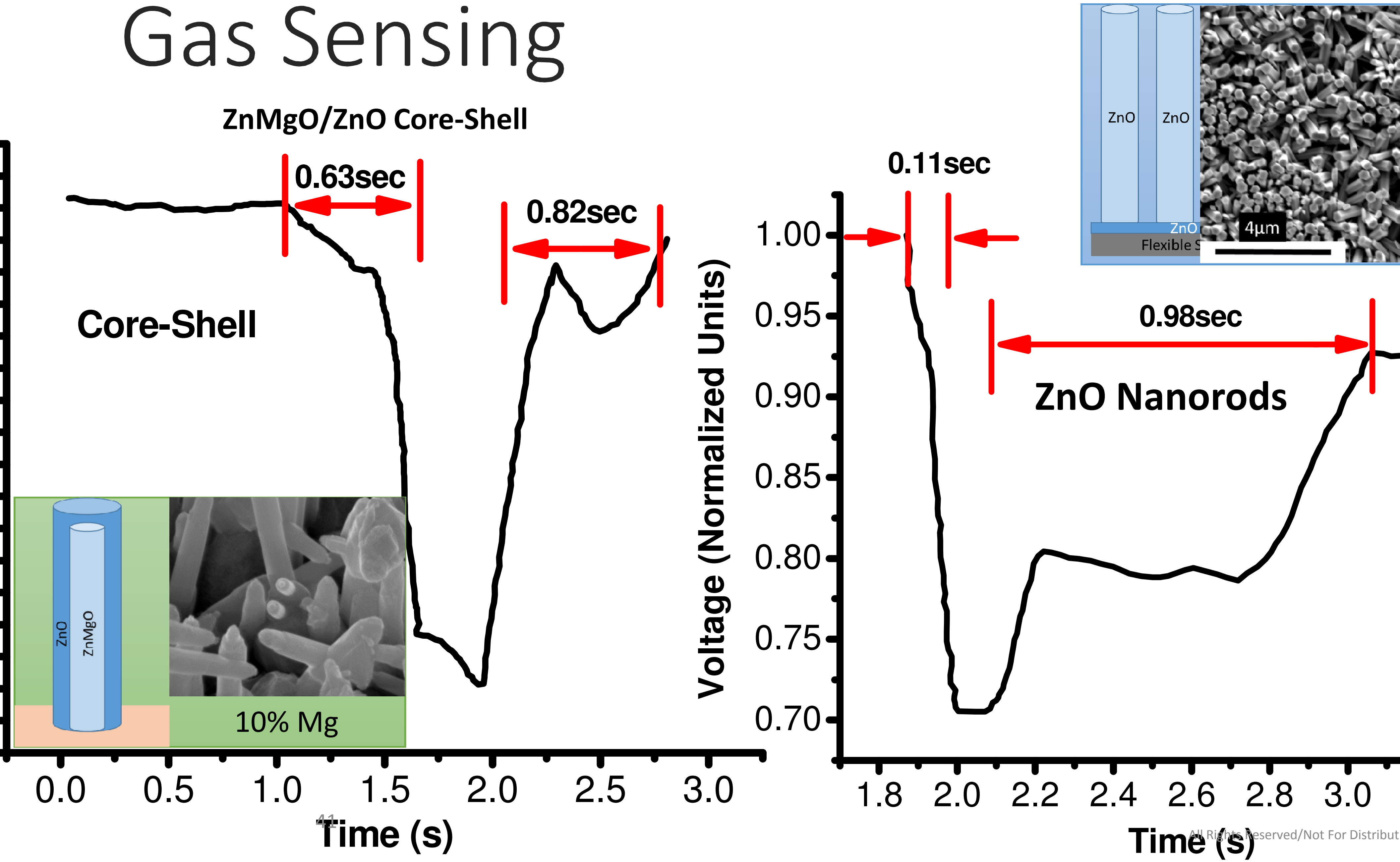


Response of ZnMgO/ZnO Core-Shell Structure





Gas Sensing



a et al.,"ZnMgO/ZnO Core-Shell Structures for Gas and UV Sensing", *Connecticut Microelectronics and Optoelectronics Consortium (CMO*
Storrs, CT, April 9, 2014.

vation Energy of Traps From Methanol Adsorp

$$t_d = \frac{1}{\sigma_n \, v_{th} \, N_C \, e^{-(E_c - E_T)/kT}}$$

.130 s for CS and, 3.3 and 5 s for NRs) is the detrapping

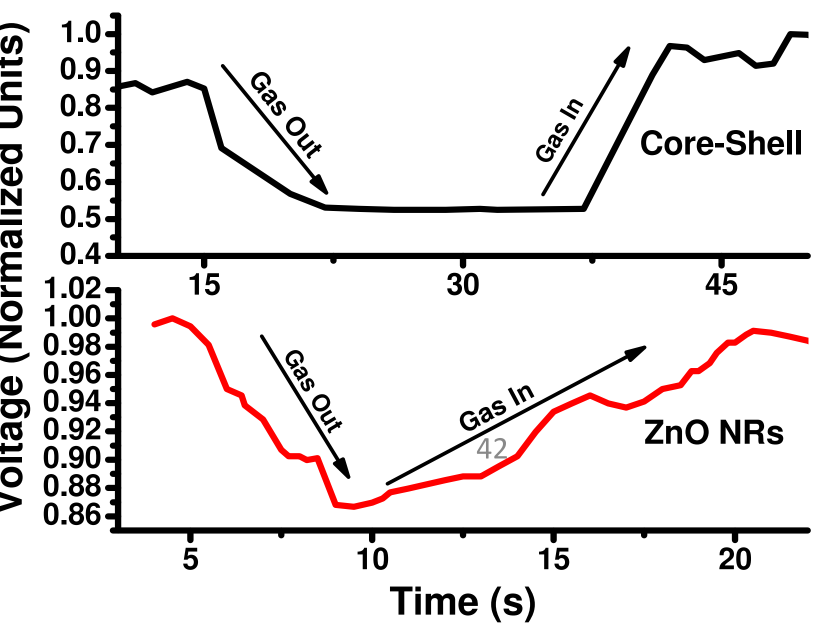
.6x10^{-13} cm^{-2} [41]) is the electron capture cross section,

hermal velocity ($\sqrt{3kT/m_e^*}$),

1x10^{18} cm^{-3}) is the effective density of states,

E_T are the conduction and trap energy levels, and m_e^* (=

or CS and 0.138 for NR) is the electron effective mass.



Activation Energy:

Core-Shell = **1.16eV**

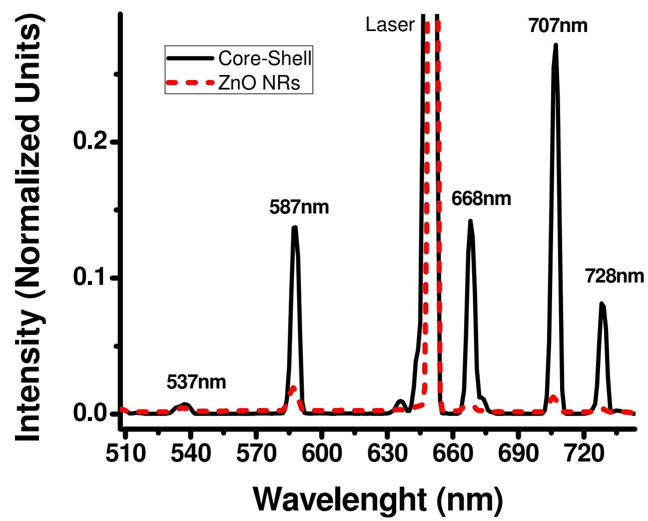
Energy Trap with Eg = 3.48eV

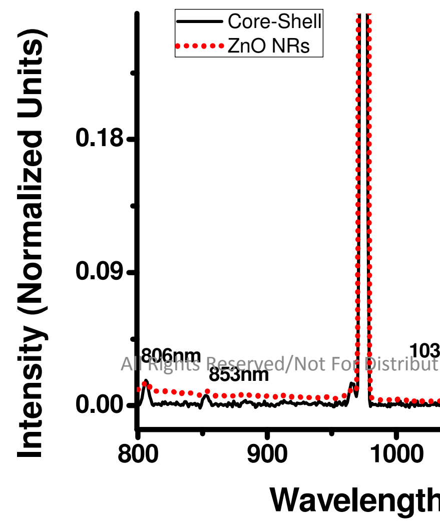
Vo **(neutral oxygen vacancies)**

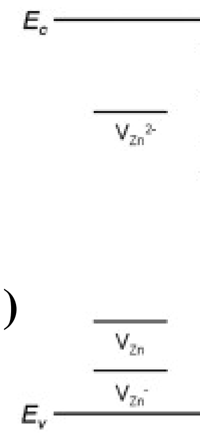
Nanorods = **1.25-1.26eV**

Energy Trap with Eg = 3.27eV

V^{+}o **(single charged oxygen vacancy)**







A.J. Dju
Progress
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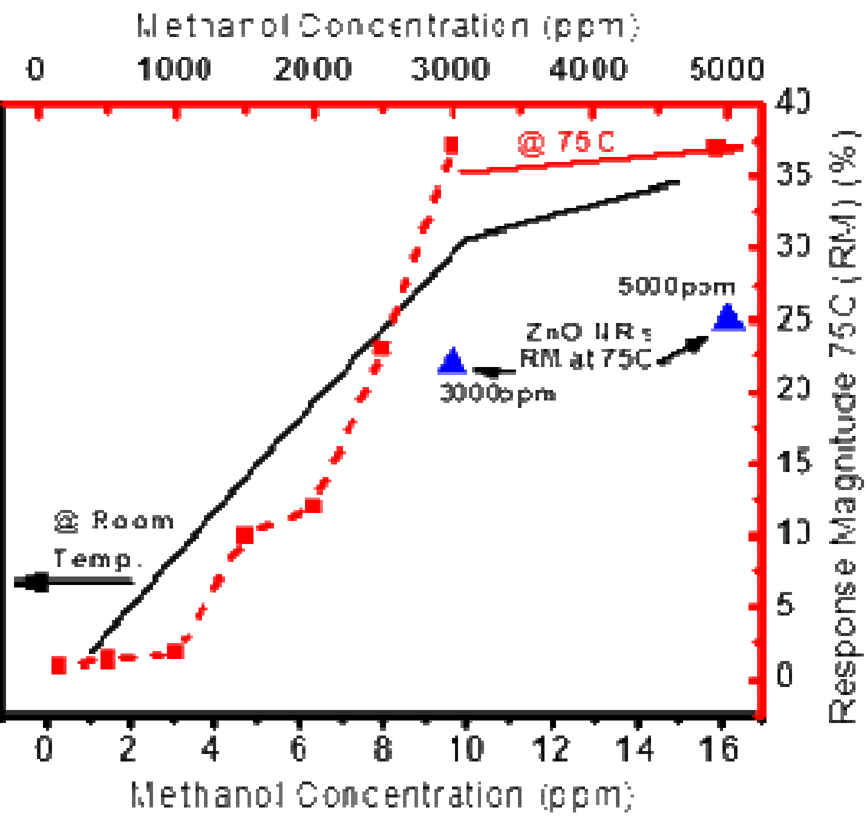
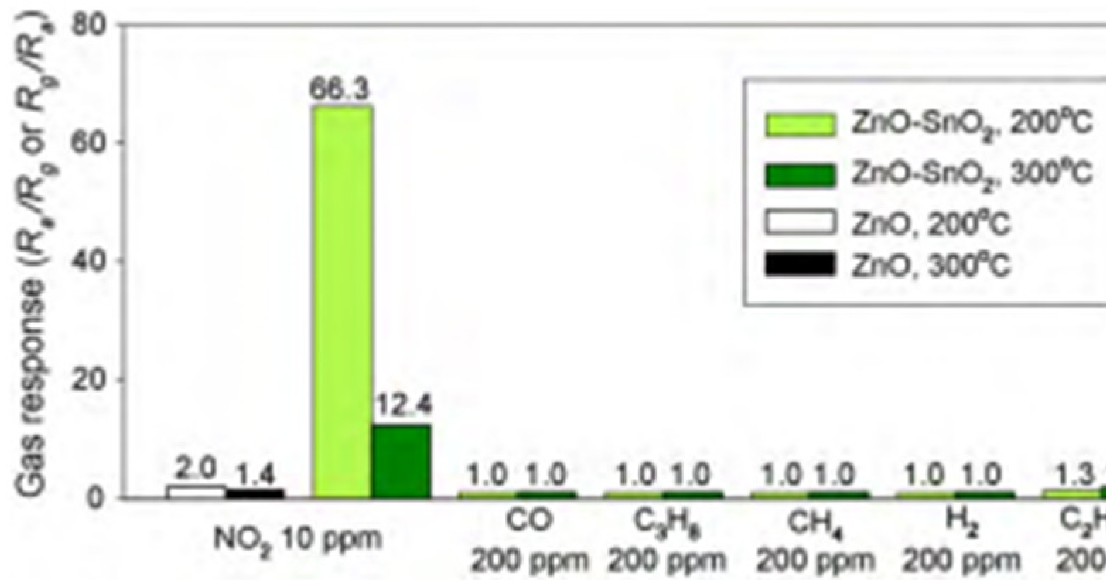
Volume 34
2010, Pag

Response Magnitude
Core-Shell vs ZnO Nanorods



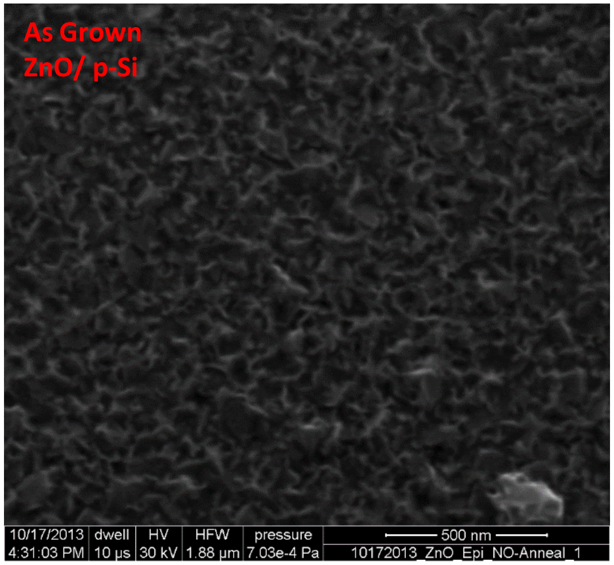
onse magnitude (RM) of ZnMgO/ZnO core-shell structure at low methanol n (solid black line with left y-axis and bottom x-axis) carried out at room p x-axis and right y-axis (red-dash line-square) shows the RM of the CS at nol concentration carried at 75 ˚C. The blue triangles are the RM for ZnO R) recorded at 75 ˚C with methanol concentration of 3000 and 5000ppm.

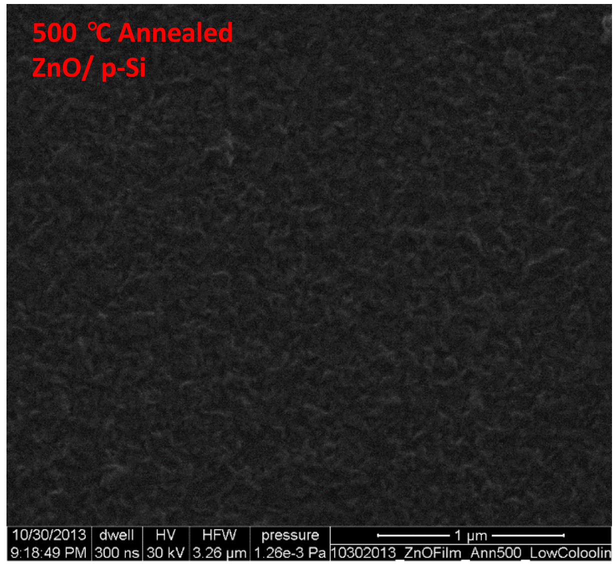


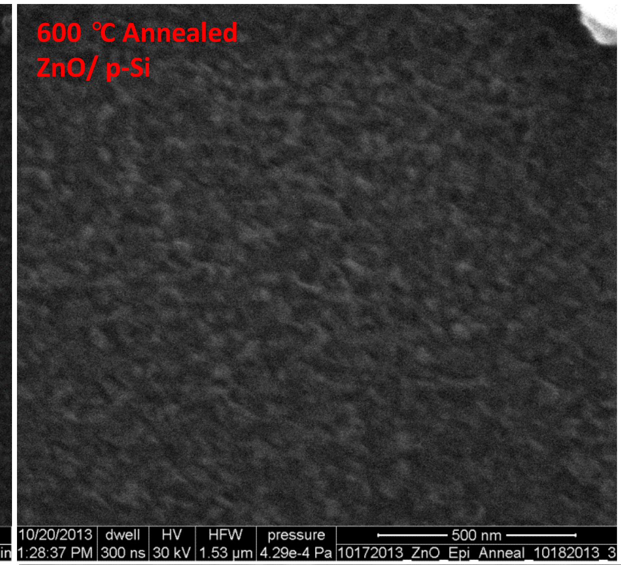
Gas responses (R_g/R_a or R_a/R_g, R_a: resistance in air and R_g: resistan to 10 ppm NO_2 and 200 ppm of CO, C_3H_8, CH_4, H_2 and C_2H_5OH at 200 a (R_g/R_a for NO_2 and R_a/R_g for other reducing gases).

S. Hwang et al. / Sensors and Actuators B 148 (2010 600

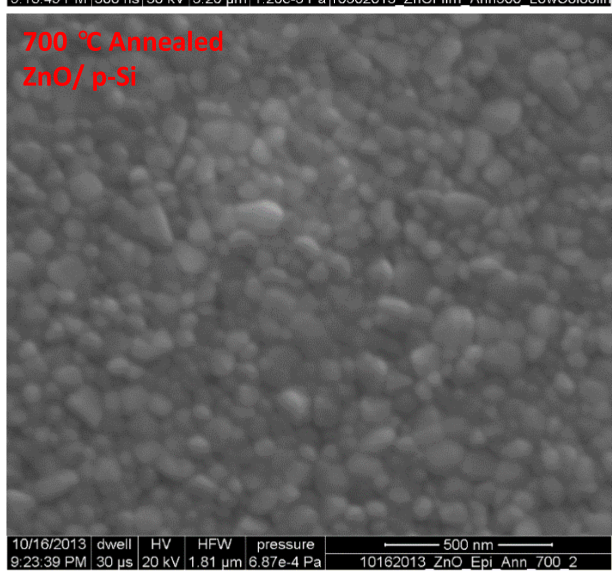
SEM Images of ZnO (thin film)/p-Si

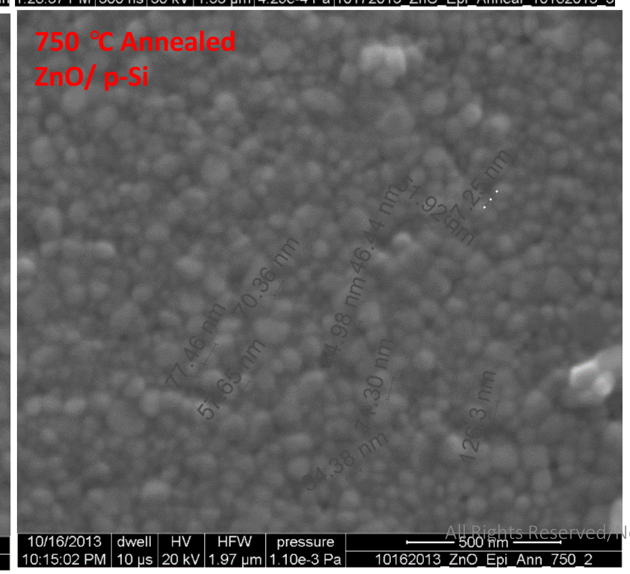






In the 500 – 600 C window, the ZnO thin film is smoother



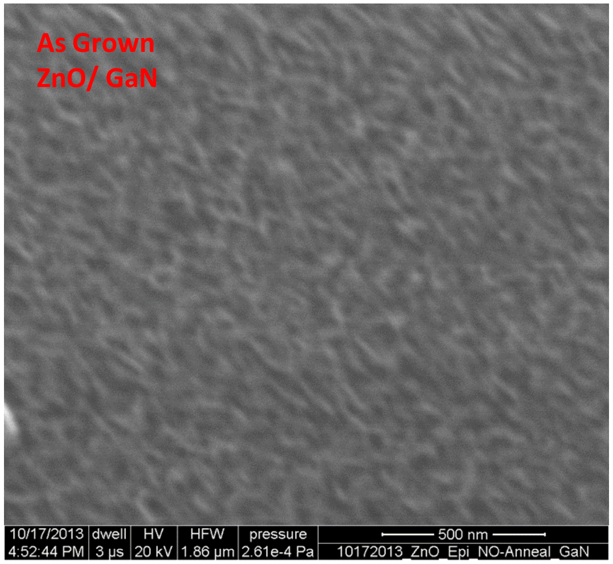


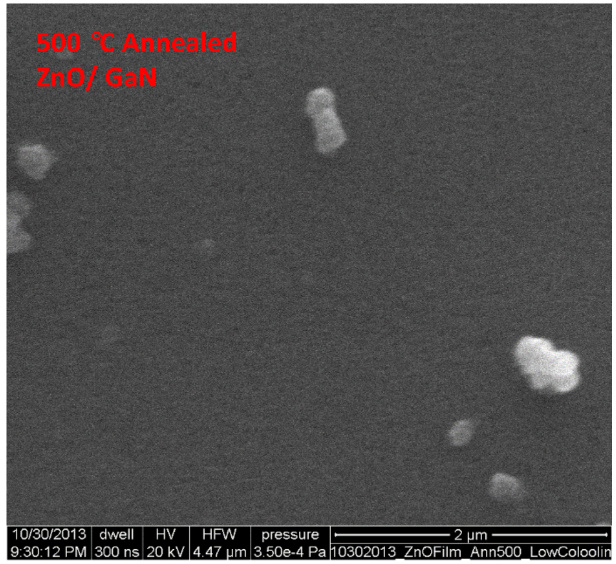
Recipe

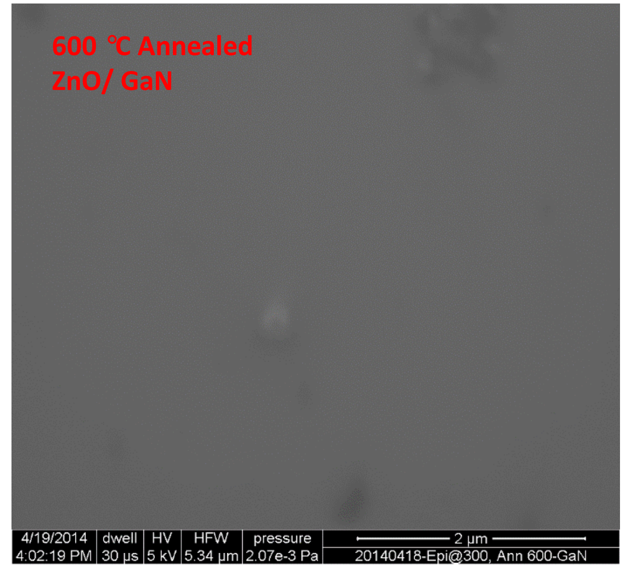
- 50sccm of DEZn
- 35sccm of N2O
- 300 C and 70 Torrs
- 20 mins

yet al., "**Optimization of Annealing Conditions for ZnO-based Thin Films Grown Using MOCVD**", *Materials Research Society (MRS) Spring M*
Francisco, CA, April 21-25, 2014. and to be published on MRS Proceedings

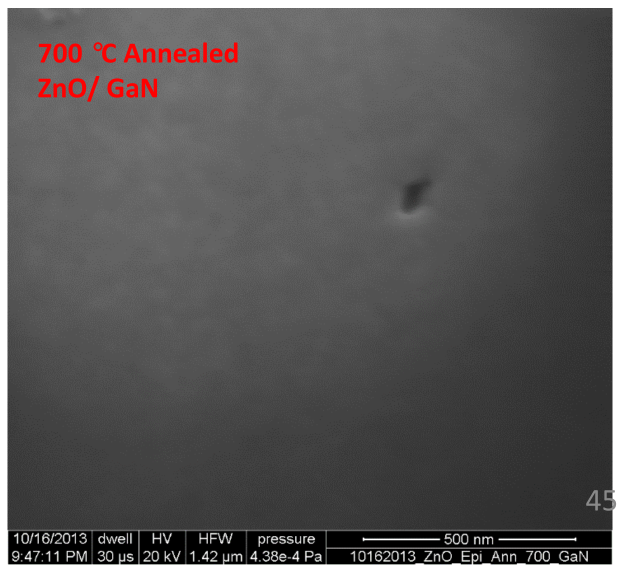
SEM Images of ZnO (thin film)/GaN

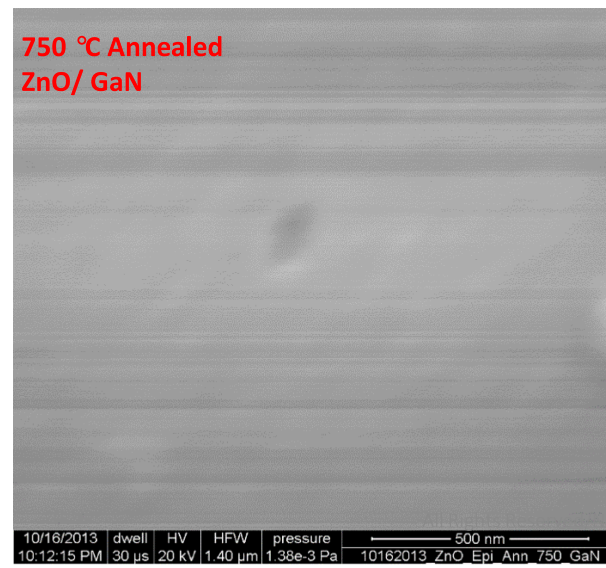






- At high annealing temperature of 700 – 750 C, the ZnO thin film is smoother (smaller RMS roughness)
- Smoother film is obtained on GaN substrates than p-Si due to smaller lattice mismatch

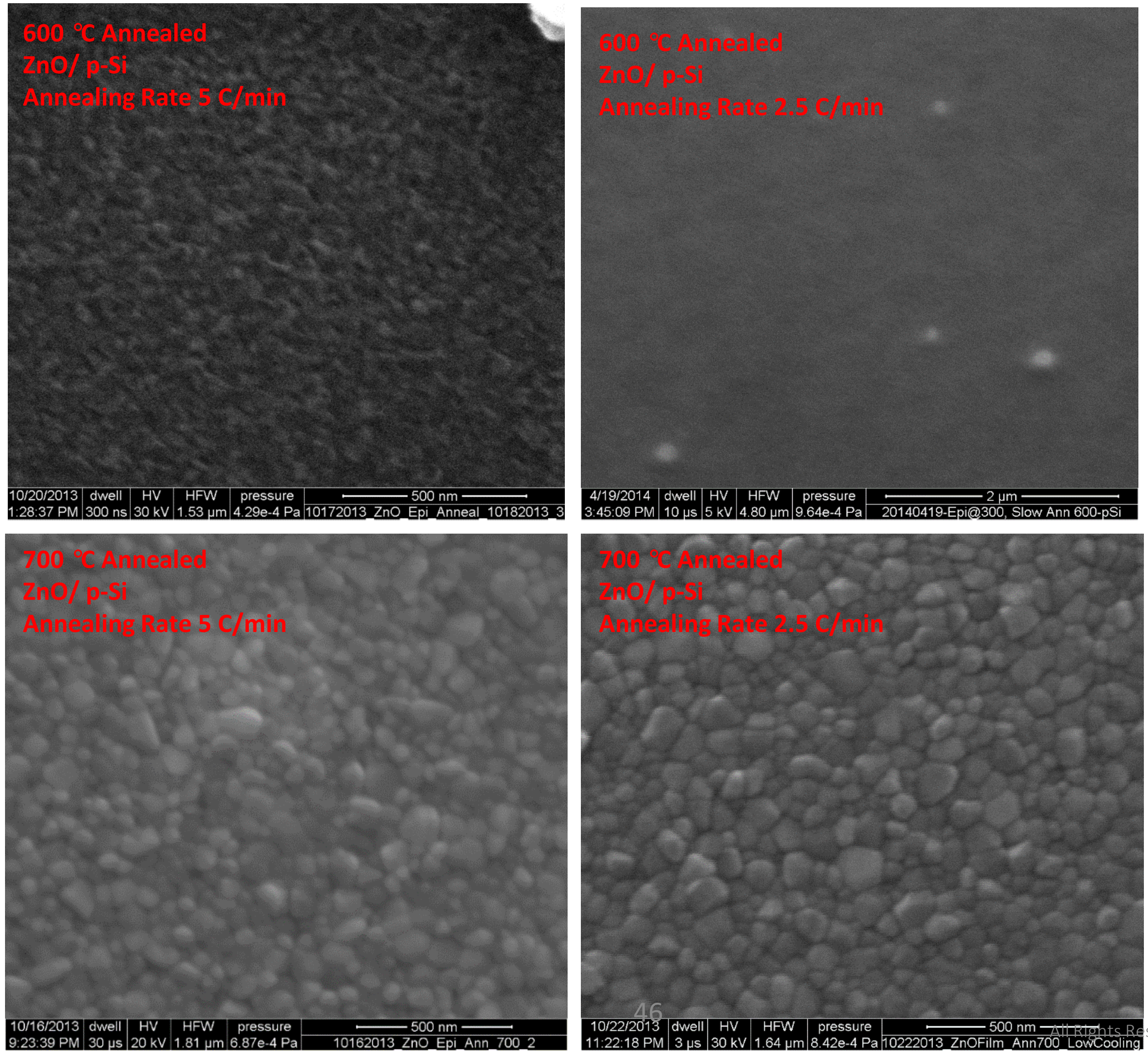




yet al., "**Optimization of Annealing Conditions for ZnO-based Thin Films Grown Using MOCVD**", *Materials Research Society (MRS) Spring I*
Francisco, CA, April 21-25, 2014. and to be published on MRS Proceedings

Slow Vs. Fast Annealing Ramp: ZnO/p-Si

- •Annealing rate did not change the surface roughness
- The grains are not due to thermal coefficient mismatch and are rather due to the annealing condition
- •High temperature causes migration of grain boundaries and coalescence of grains [Lee et al., J. of Luminescence, 129 (2009) 148-152]



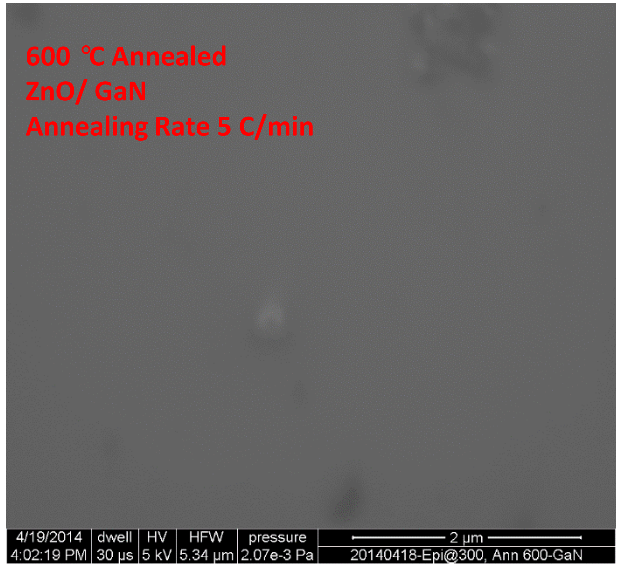
yet al., "**Optimization of Annealing Conditions for ZnO-based Thin Films Grown Using MOCVD**", *Materials Research Society (MRS) Spring M*
Francisco, CA, April 21-25, 2014. and to be published on MRS Proceedings

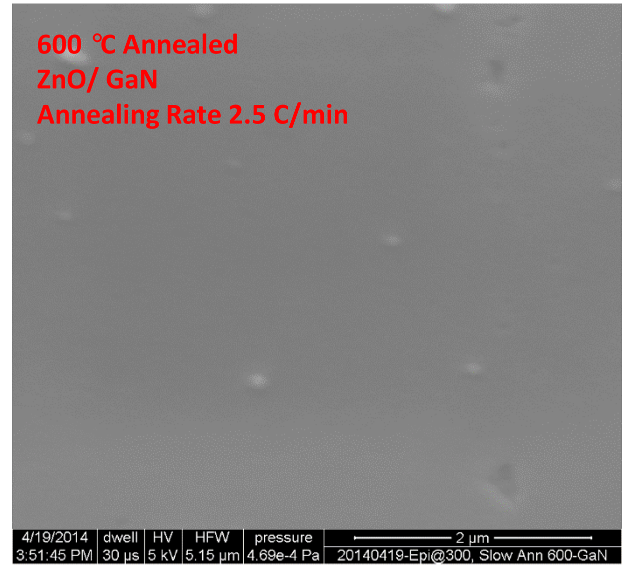
Slow Vs. Fast Annealing Ramp: ZnO/GaN

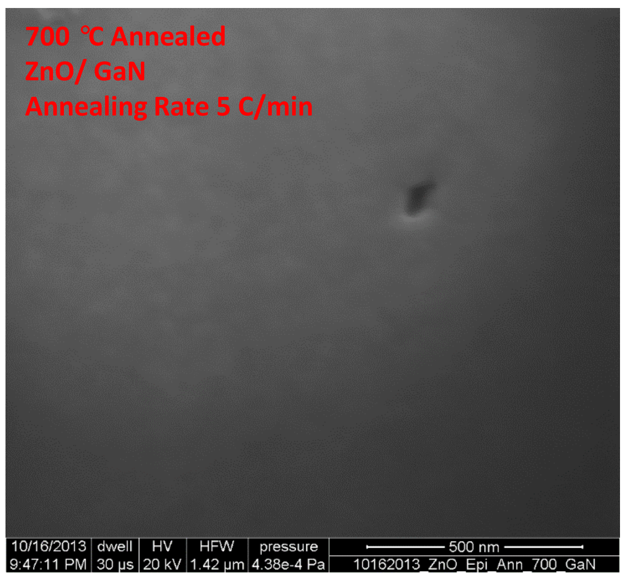
- Annealing rate did not change the surface roughness

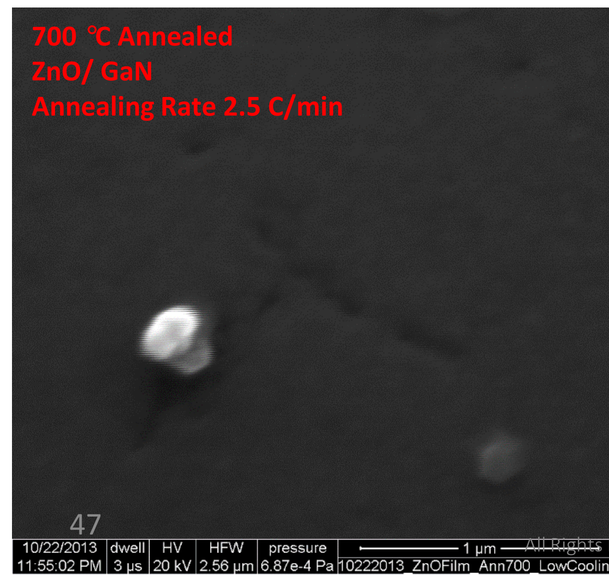
- The grains are not due to thermal coefficient mismatch and are rather due to the annealing condition

- High temperature causes migration of grain boundaries and coalescence of grains [Lee et al., J. of Luminescence, 129 (2009) 148-152]









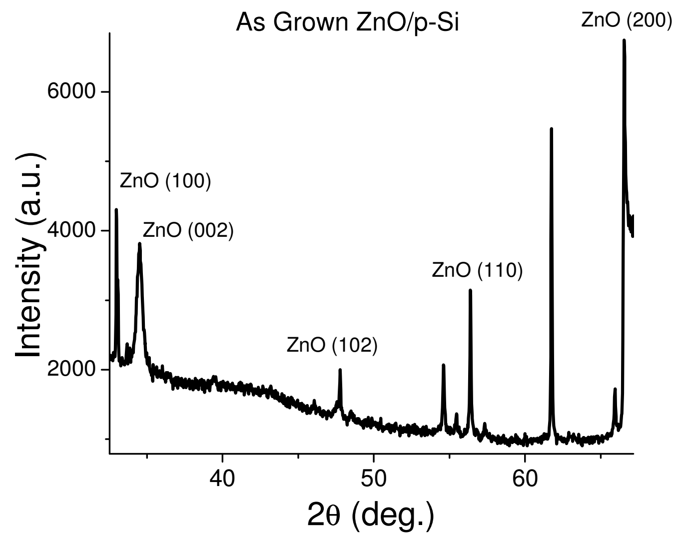
yet al., "**Optimization of Annealing Conditions for ZnO-based Thin Films Grown Using MOCVD**", *Materials Research Society (MRS) Spring M*
Francisco, CA, April 21-25, 2014. and to be published on MRS Proceedings

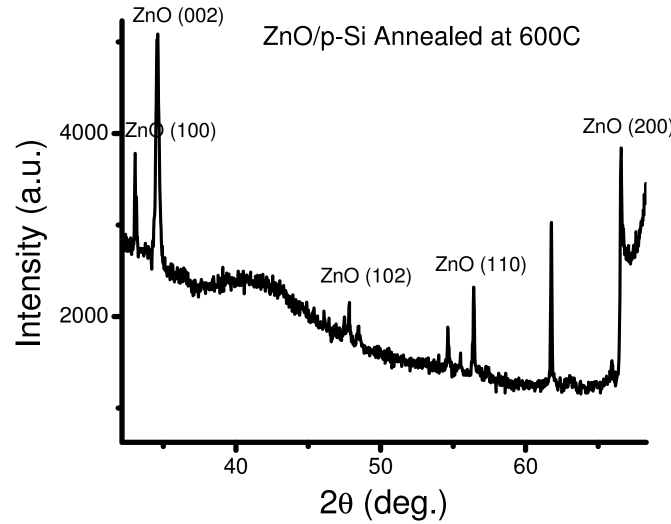
Surface Roughness Vs. Annealing Temperature

Substrate	Annealing	Surface Roughness
p-Si	As grown	Fine grains
p-Si	600 °C	Smooth surface
p-Si	700 °C	Grain size: 36-154 nm
p-Si	700 °C (slower ramp)	Grain size: 40-153 nm
p-Si	750 °C	Grain size: 34-140 nm
GaN	As grown	Fine grains
GaN	700 °C	Very smooth
GaN	700 °C (slower ramp)	Very smooth
GaN	750 °C	Very smooth

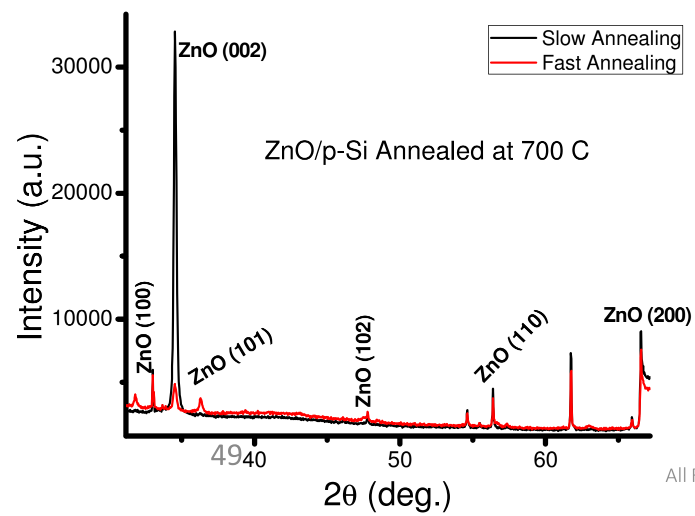
yet al., "**Optimization of Annealing Conditions for ZnO-based Thin Films Grown Using MOCVD**", *Materials Research Society (MRS) Spring M*
Francisco, CA, April 21-25, 2014. and to be published on MRS Proceedings

Crystalline Structure of ZnO (thin film)/p-Si





- ZnO becomes more single crystalline for higher temperature annealing at a slower rate
- High temperature causes migration of grain boundaries and coalescence of grains [Lee et al., J. of Luminescence, 129 (2009) 148-152]



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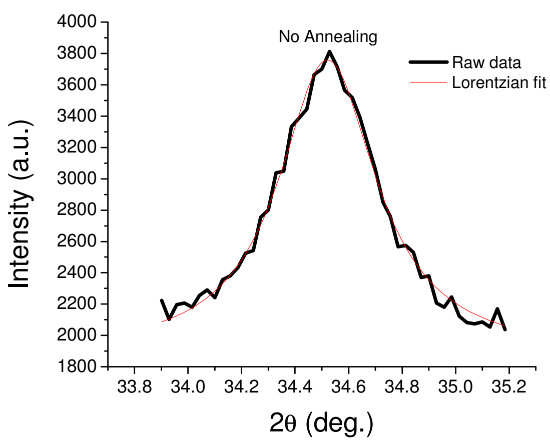
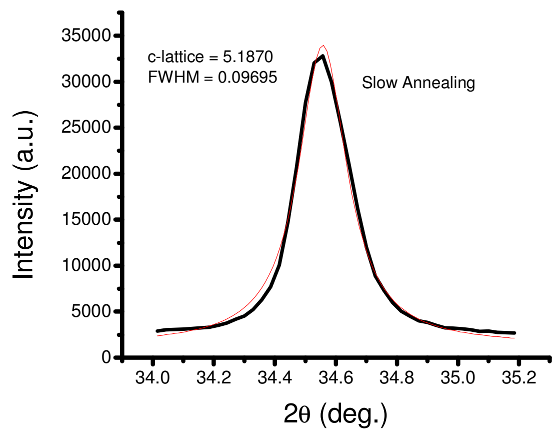
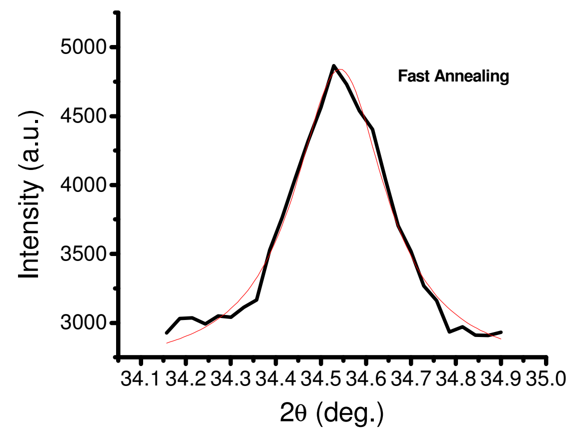
Francisco, CA, April 21-25, 2014. and to be published on MRS Proceedings

Crystal Quality of ZnO (thin film)/p-Si

ZnO/ p-Si	As-Grown	500C Annealed	600C Annealed	700C Slow Annealed	700C Fast Annealed
c-lattice (Å)	5.1921	5.1906	5.1820	5.1870	5.1891
a-lattice (Å)	3.2430	3.2430	3.2406	3.1792	3.2417
Misfit Strain	67.47%	67.47%	67.59%	70.83%	67.53%
FWHM (deg)	0.2225	0.1279	0.1280	0.09695	0.1239





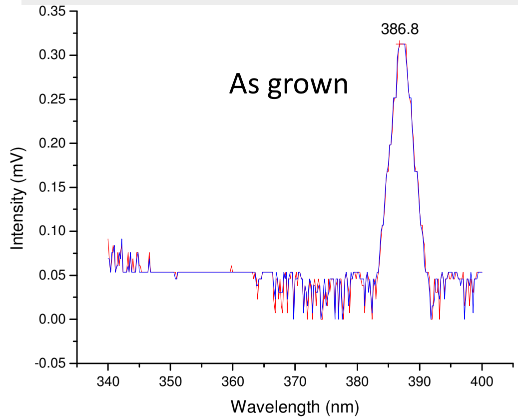


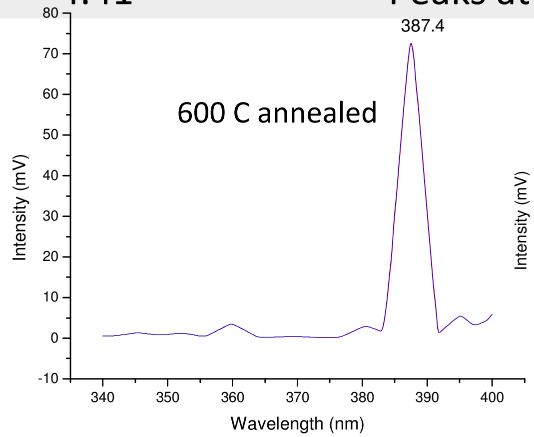
- The FWHM decreases with increasing annealing temperature
- Crystal quality can be improved by slowing down the annealing rate

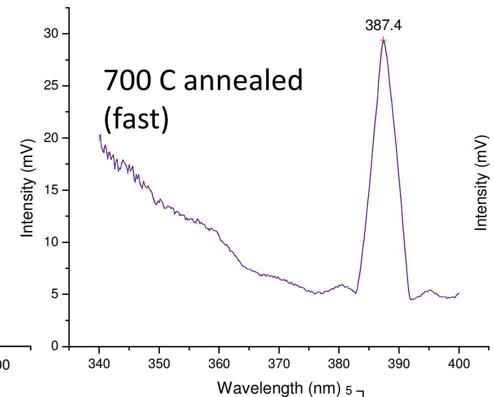
yet al., "**Optimization of Annealing Conditions for ZnO-based Thin Films Grown Using MOCVD**", *Materials Research Society (MRS) Spring I*
Francisco, CA, April 21-25, 2014. and to be published on MRS Proceedings

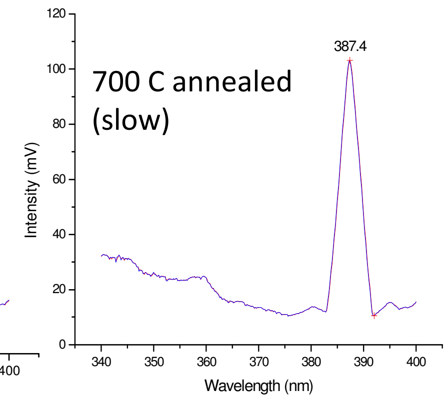
Optical Quality of ZnO (thin film)/p-Si

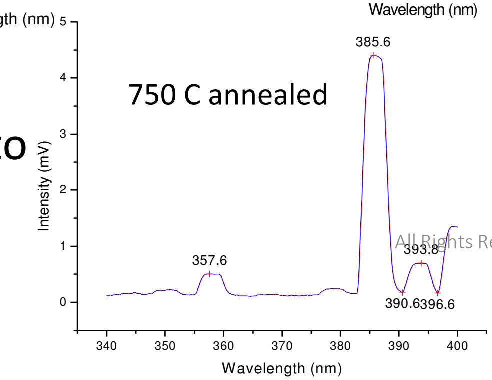
Anneal	Peak Position (nm)	Relative Peak Intensity	Other peaks	FWHM (nm)
none	386.8	0.31		5.2108
600 °C	387.4	72.54		4.377
700 °C	387.4	29.36	Broad peak at lower wavelengths	5.2107
700 °C (slow)	387.4	103.12	Small peak at 359.4 nm	4.79
750 °C	385.6	4.41	Peaks at 357.6, 393.8 nm	4.377







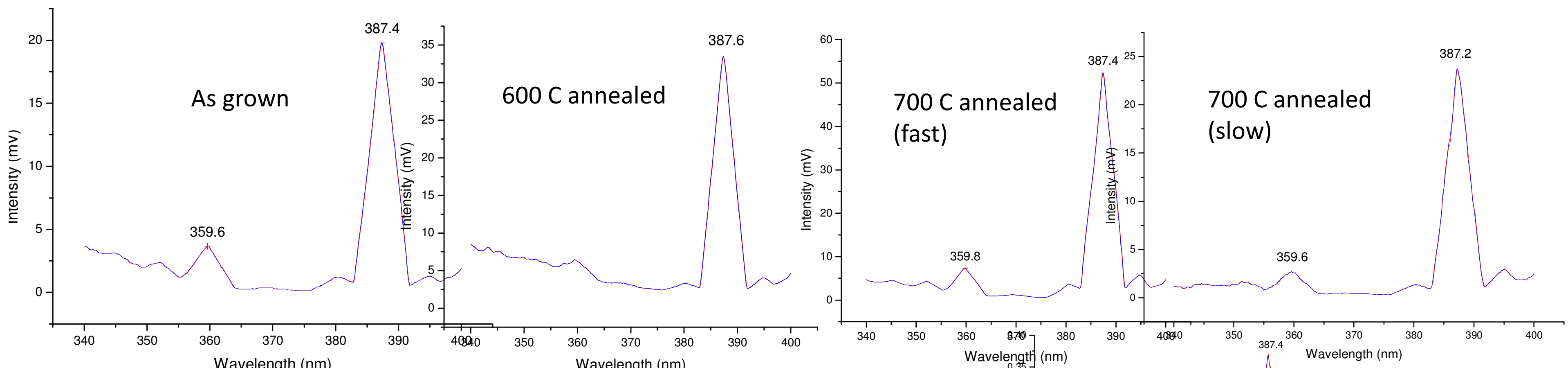




- •Near band-edge (NBE) energy (~387 nm) is the dominant peak
- •The peak at ~358 nm (3.45 eV) corresponds to electronic band to band transition [*G.H. Lee et al., Thin Solid Films 386 (2001) 117-120*]
- • Samples annealed at 600 C has minimum defects/ impurity
- • Slower annealing rate results in better optical quality

Optical Quality of ZnO (thin film)/GaN

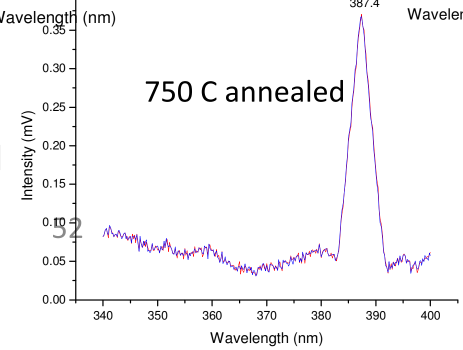
Anneal	Peak Position (nm)	Relative Peak Intensity	Other peaks	FWHM (nm)
none	387.4	19.84	359.6 nm	4.5854
600 °C	387.6	33.478	359.6 nm	4.585
700 °C	387.4	52.44	359.8 nm	4.7938
700 °C (slow)	387.2	23.77	359.6 nm	4.5854
750 °C	387.4	0.37		4.7939



•The peak at ~358 nm (3.45 eV) corresponds to electronic band to band transition [*G.H. Lee et al., Thin Solid Films 386 (2001) 117-120*]

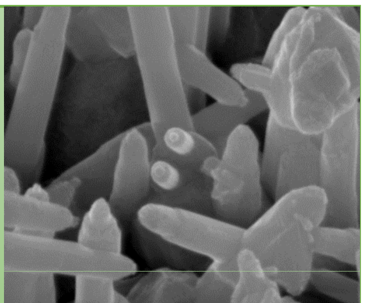
• Optical quality deteriorates for annealing temperatures > 700 C.

• Slower annealing results in better optical quality



Summary

gO/ZnO Core-Shell

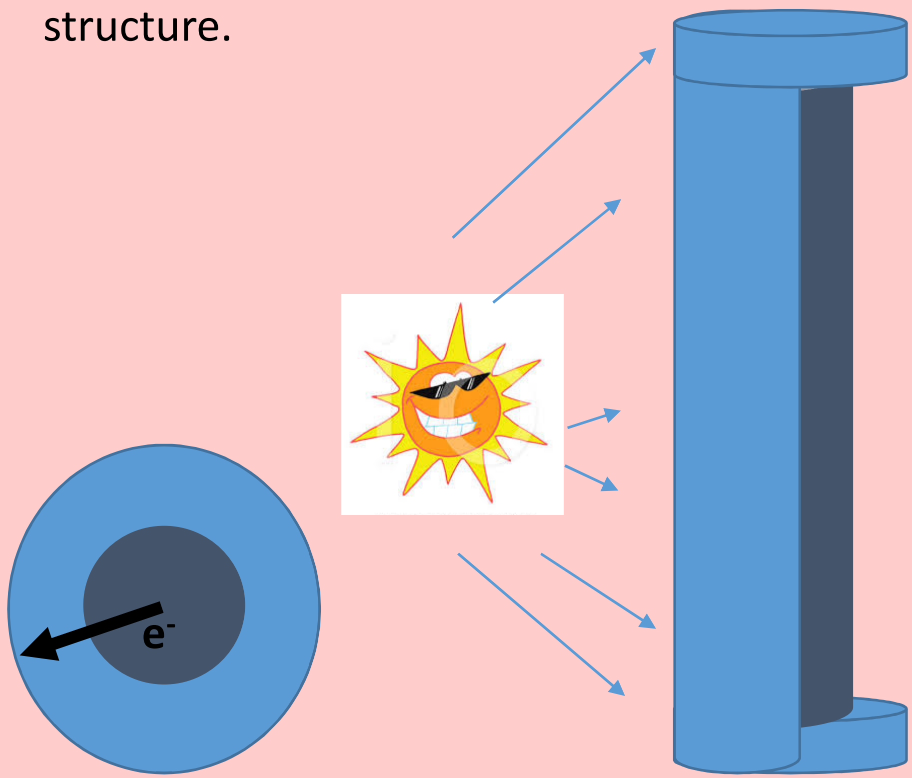


10% Mg

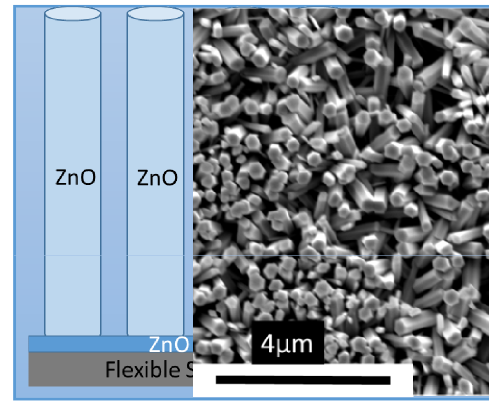
ore)	ZnO (Shell)
.1868	C-lattice 5.1849
0823	FWHM 0.0427

Magnitude of 1 – 37%
nol Concentration of
pm

- Sun Light is Absorbed along the NW (**axial**)
- While collection of e^- depends **radially**
- Therefore, **less recombination**
- And **Higher Absorption Coeff**. due to size of structure.



ZnO Nanorods



ZnO NRs
C-lattice 5.192
FWHM 0.0552

Sensitivity of 5 - 6 at R
Temperature For Meth
Concentration of XX

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