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Effect of Growth Conditions on Morphology and Composition of Aligned ZnO Nanorod Arrays

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Symposium K: Zinc Oxide and Related Materials
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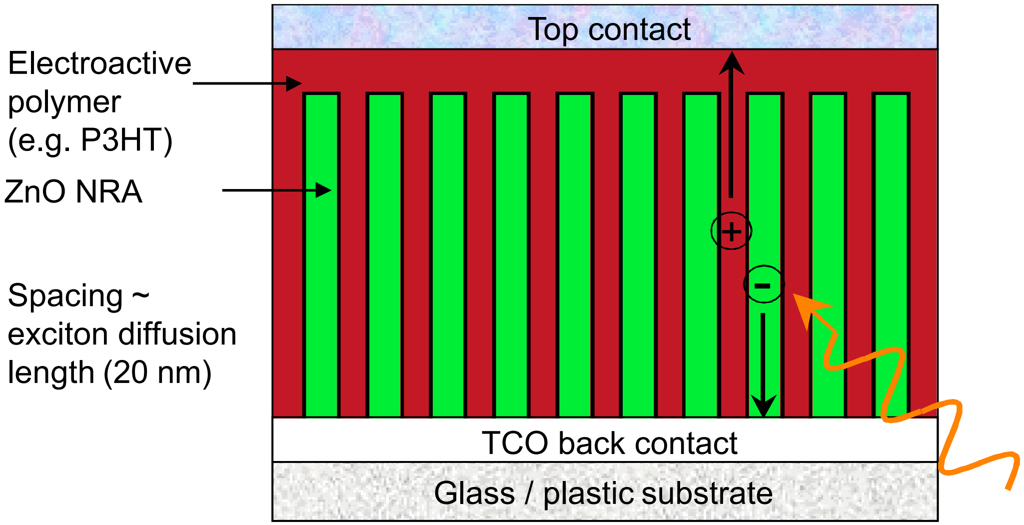
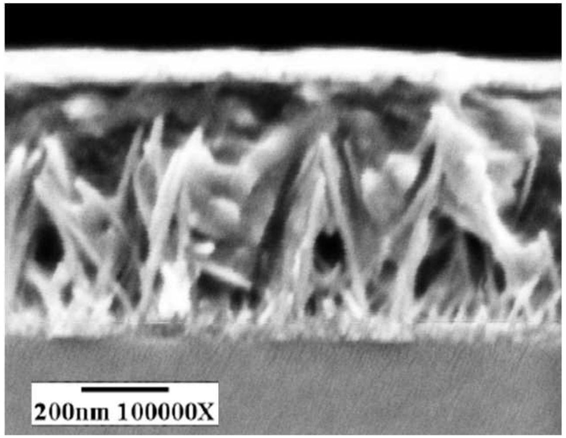
Polymer-ZnO NRA PV Cells



Proposed “ideal structure”



Current best device
Eff = 0.53%

D.C. Olson et al., *Thin Solid Films* **496**, 26 (2006)

<u>Advantages of ZnO NRA electron transport layer:</u>

- Increased interfacial area compared to bilayer devices
- Good electrical contact to bottom electrode
- High electron mobility (up to 10 cm^2 / V s)
- Maximize carrier collection by varying NRA spacing
- Modify band structure through judicious choice of materials

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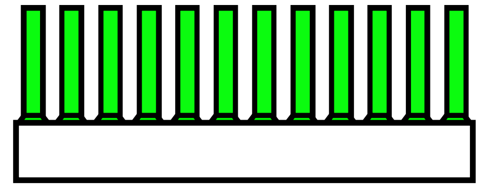
Aligned ZnO Nanorod Array Synthesis

Deposit seed layer on substrate

1. Clean substrates (sonication, ozone)
2. Coat substrate with 5mM $Zn(OAc)_2$ in EtOH
3. Leave on substrate for 25 s
4. Rinse with EtOH and blow dry
5. Repeat steps 1-3 4 times
6. Anneal in oven at 350 °C for 20 min
7. Repeat steps 1-5

L. E. Greene et al., *Nano. Lett.* **5**, 1231 (2005)

Grow nanorods in aqueous solution



HMT (pH 6.5) recipe:

1. 25 mM $Zn(NO_3)_2$ + HMT in water
2. Submerge seeded substrate in growth solution
3. Place in oven at 92.5 °C for 2 hr

L. E. Greene et al., *Nano. Lett.* **5**, 1231 (2005)

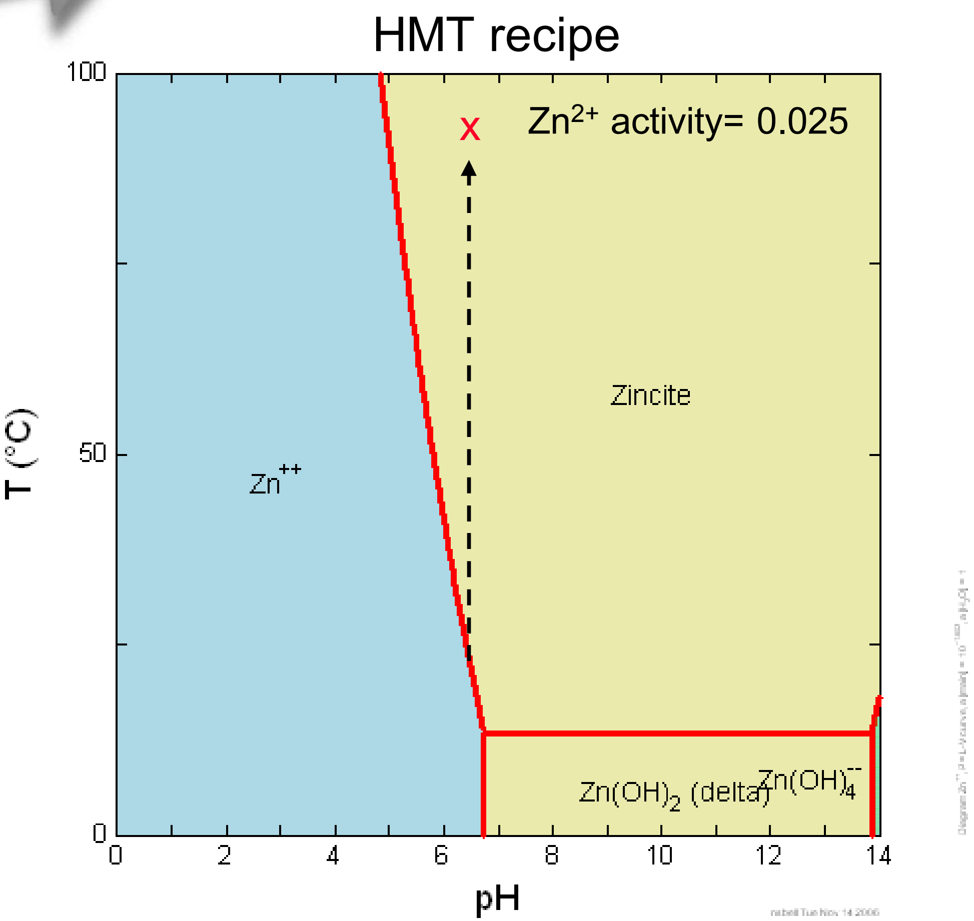
NaOH (pH 13.2) recipe:

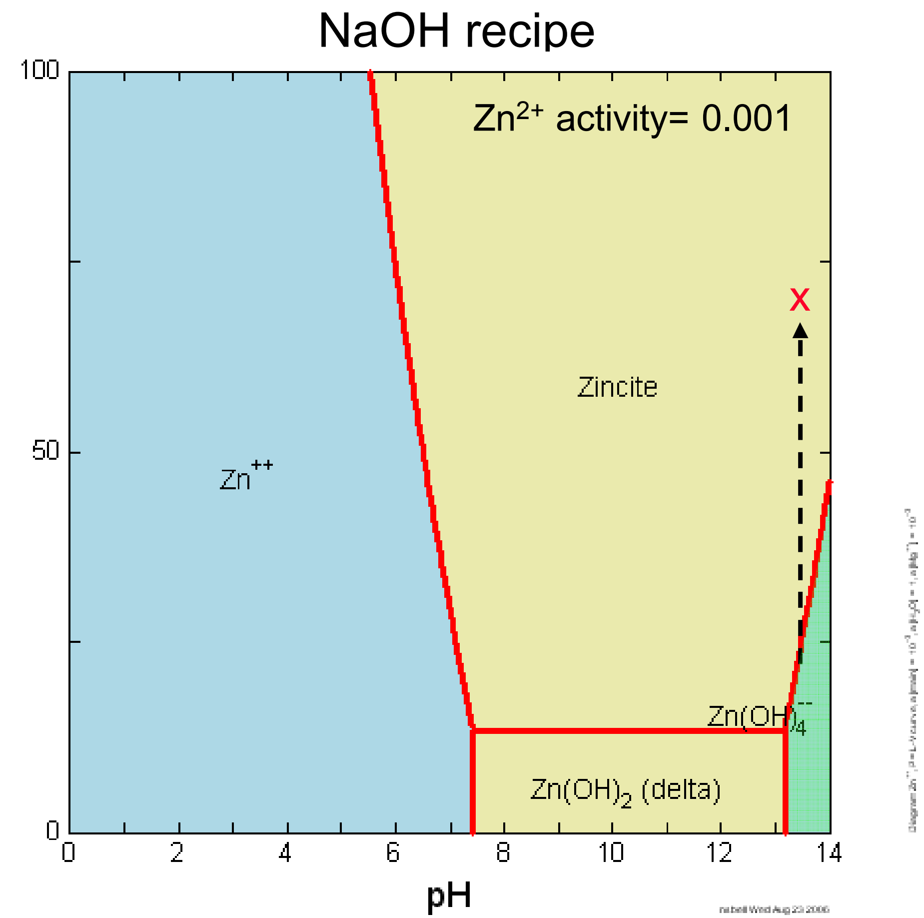
1. 1 mM $Zn(NO_3)_2$ + 90 mM NaOH in water
2. Submerge seeded substrate in growth solution
3. Place in oven at 70 °C for 2 hr

C. L. Peterson et al., *Langmuir* **20**, 5114 (2004)

- How does solution pH affect ZnO NRA morphology?

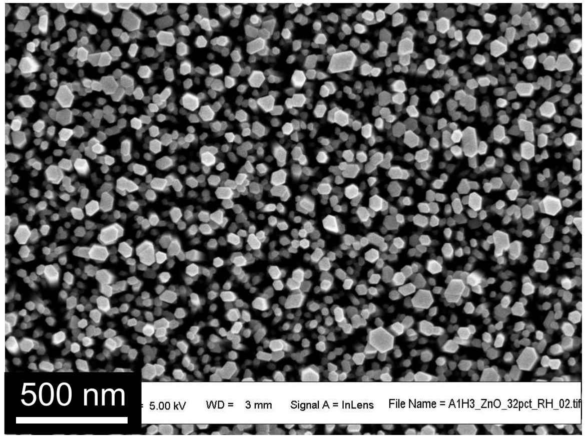
Zn Speciation Diagram

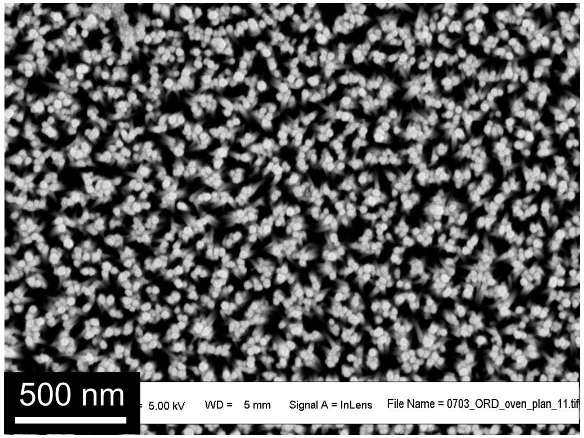




- ZnO deposition caused by decreased solubility at high temperatures
- Soluble Zn species depends on solution pH
- Effects of deposition kinetics?

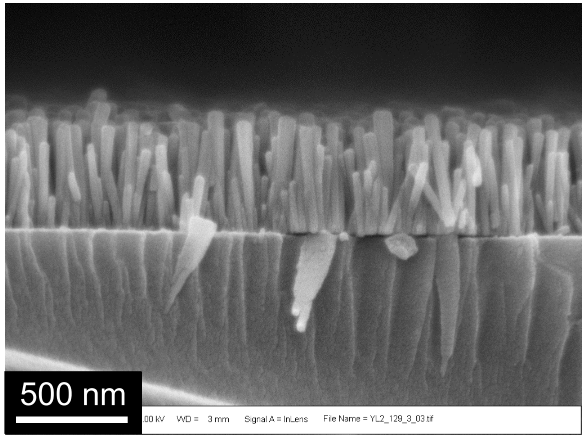
Effect of Growth pH

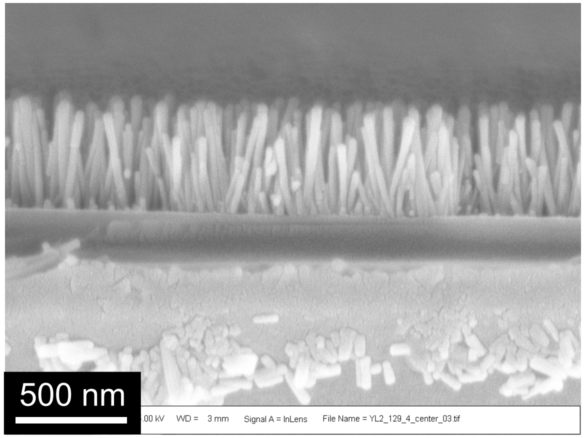




HMT, pH 6.5, 106 min

NaOH, pH 13.2, 40 min





- Highly aligned ZnO NRAs due to seeding process
- NaOH recipe --> smaller diameter, sparser surface coverage
- Possible reason: NaOH recipe has 2.5 x deposition rate

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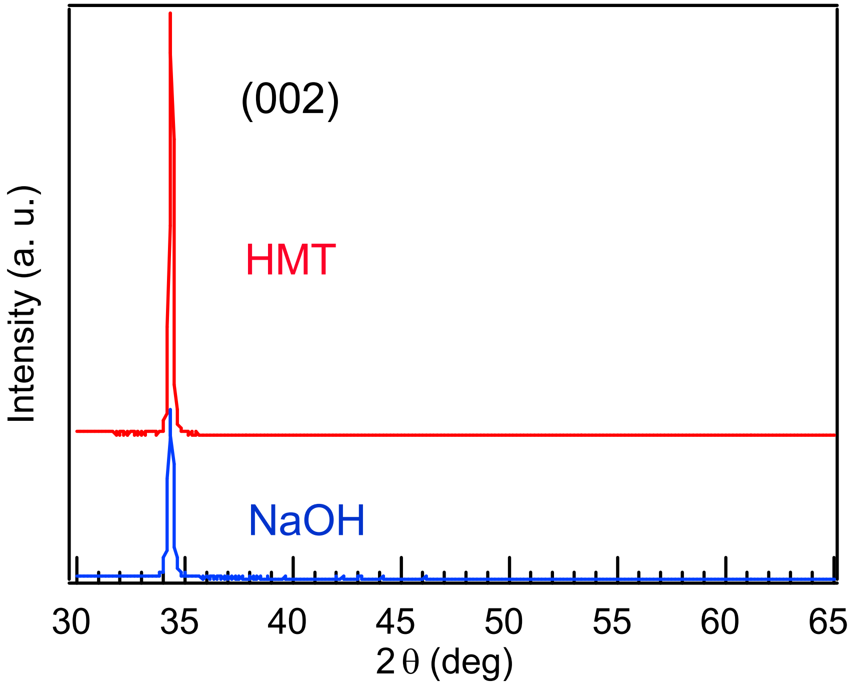
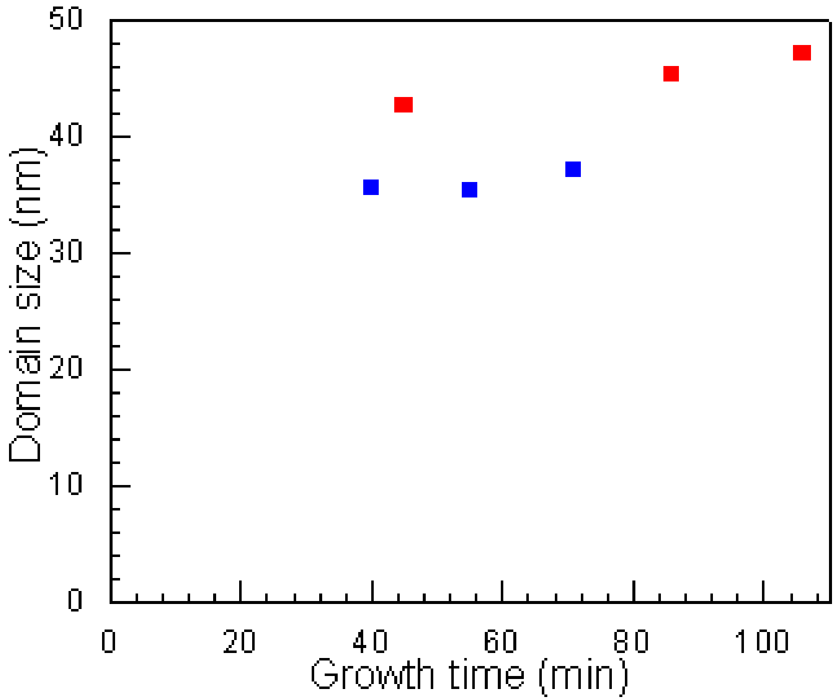
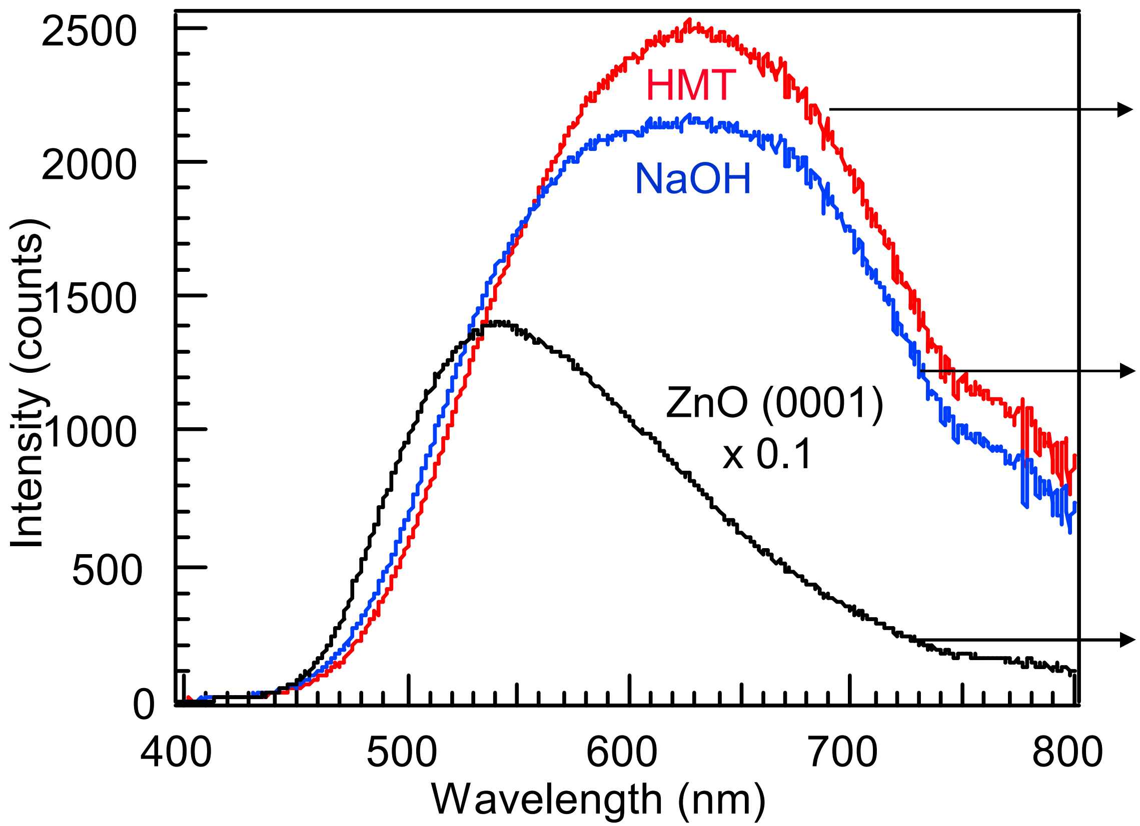
XRD of ZnO Nanorod Arrays

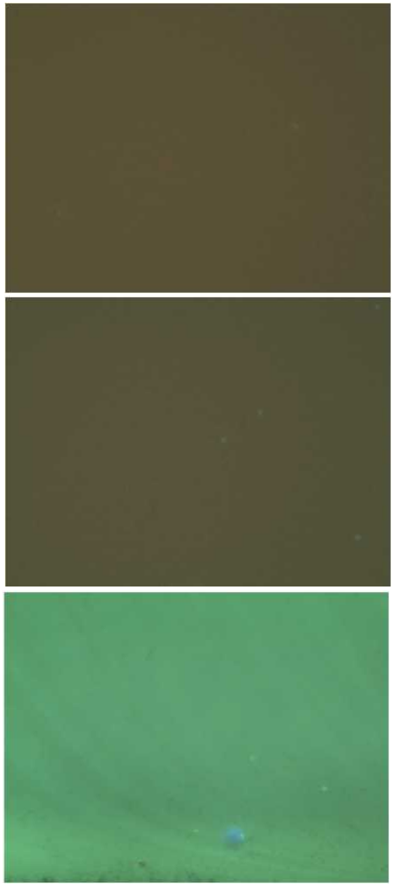




- Only (002) peak present--highly aligned nanorods
- HMT / NaOH peak area ratio ~ 1.9
- d_{HMT} ~ 45 nm, d_{NaOH} ~ 35 nm, $(d_{HMT} / d_{NaOH})^2$ ~ 1.7
- Similar # nanorods / area, different separation
- UV-vis absorption spectra agrees with XRD data

PL Spectra of ZnO Nanorod Arrays



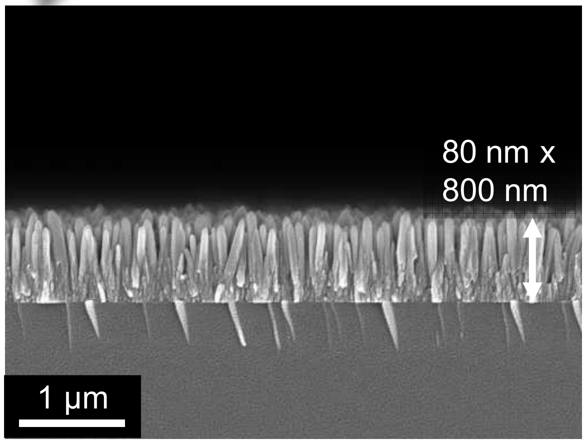


L. E. Greene et al., *Angew. Chem. Int. Ed.* **42**, 3031 (2003)
J. W. P. Hsu et al., *Appl. Phys. Lett.* **88**, 252103 (2006)

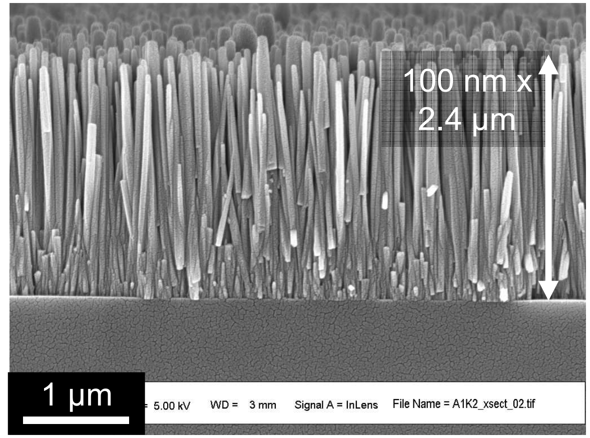
- ZnO (0001): λ = 540 nm (oxygen vacancy)
- ZnO NRA: λ = 620 nm (oxygen excess)

Effect of DAP Concentration

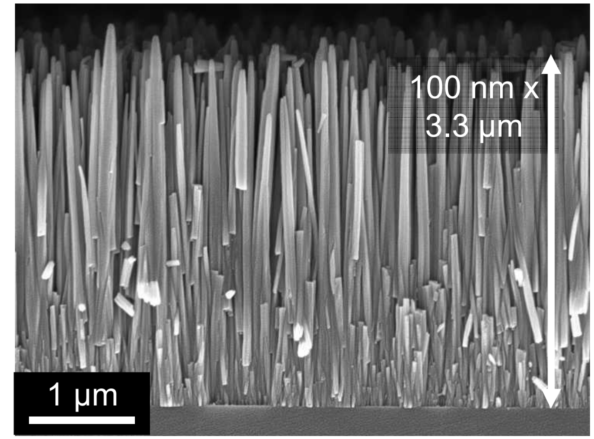
HMT recipe, growth time = 115 min



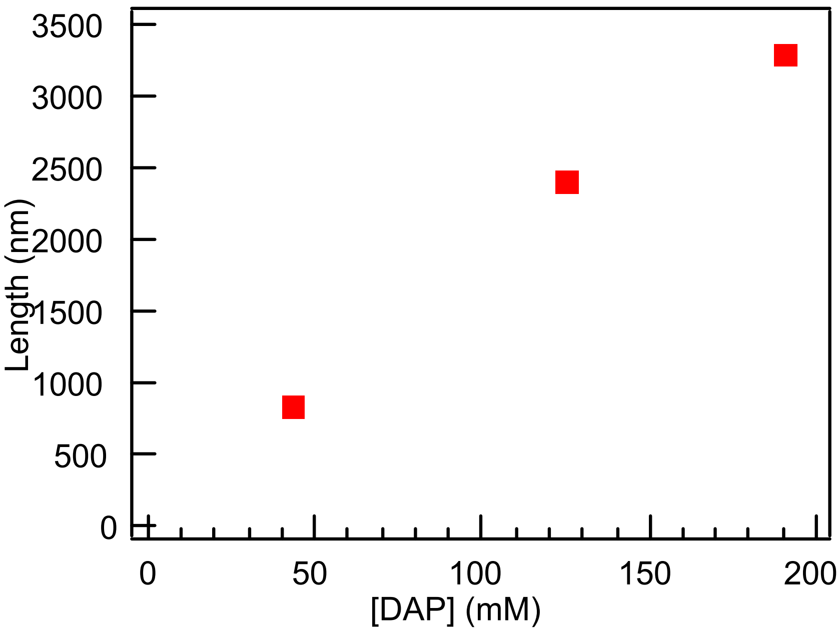
43 mM DAP, pH = 10.5



125 mM DAP, pH = 11.2



190 mM DAP, pH = 11.8

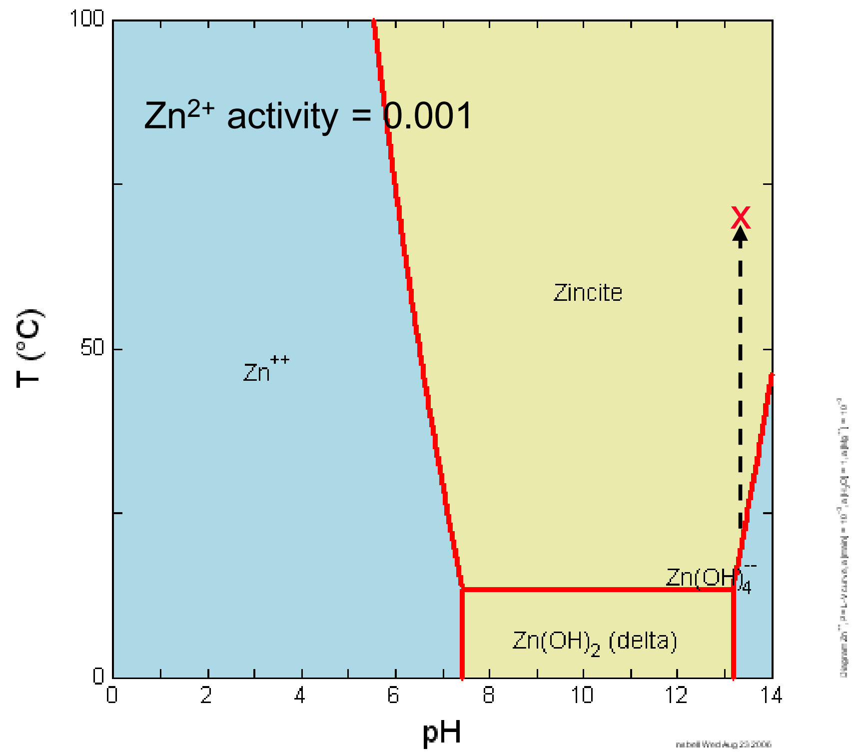


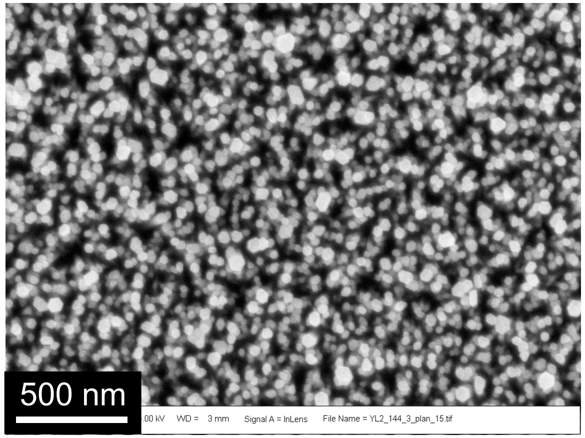
- Increased rod diameter, length, and tapering with increasing [DAP]
- Length proportional to [DAP]
- PL identical to nanorods w/ HMT recipe
- DAP chelates Zn^{2+}, reduces precipitates
- Regulation of ZnO deposition?

$Zn_{1-x}Mg_xO$ NRA Synthesis

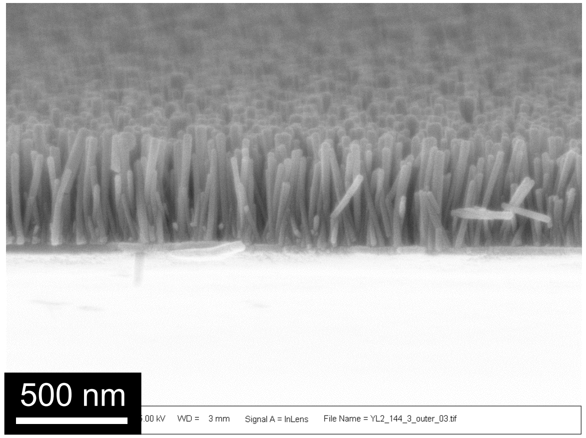
D.C. Olson et al., *Adv. Func. Mat.*, in press

Basic recipe + $Mg(NO_3)_2$





0.1 mM $Mg(NO_3)_2$, 85 min



- NRA synthesized with low $[Mg(NO_3)_2]$
- Low Mg^{2+} solubility --> low Mg substitution?

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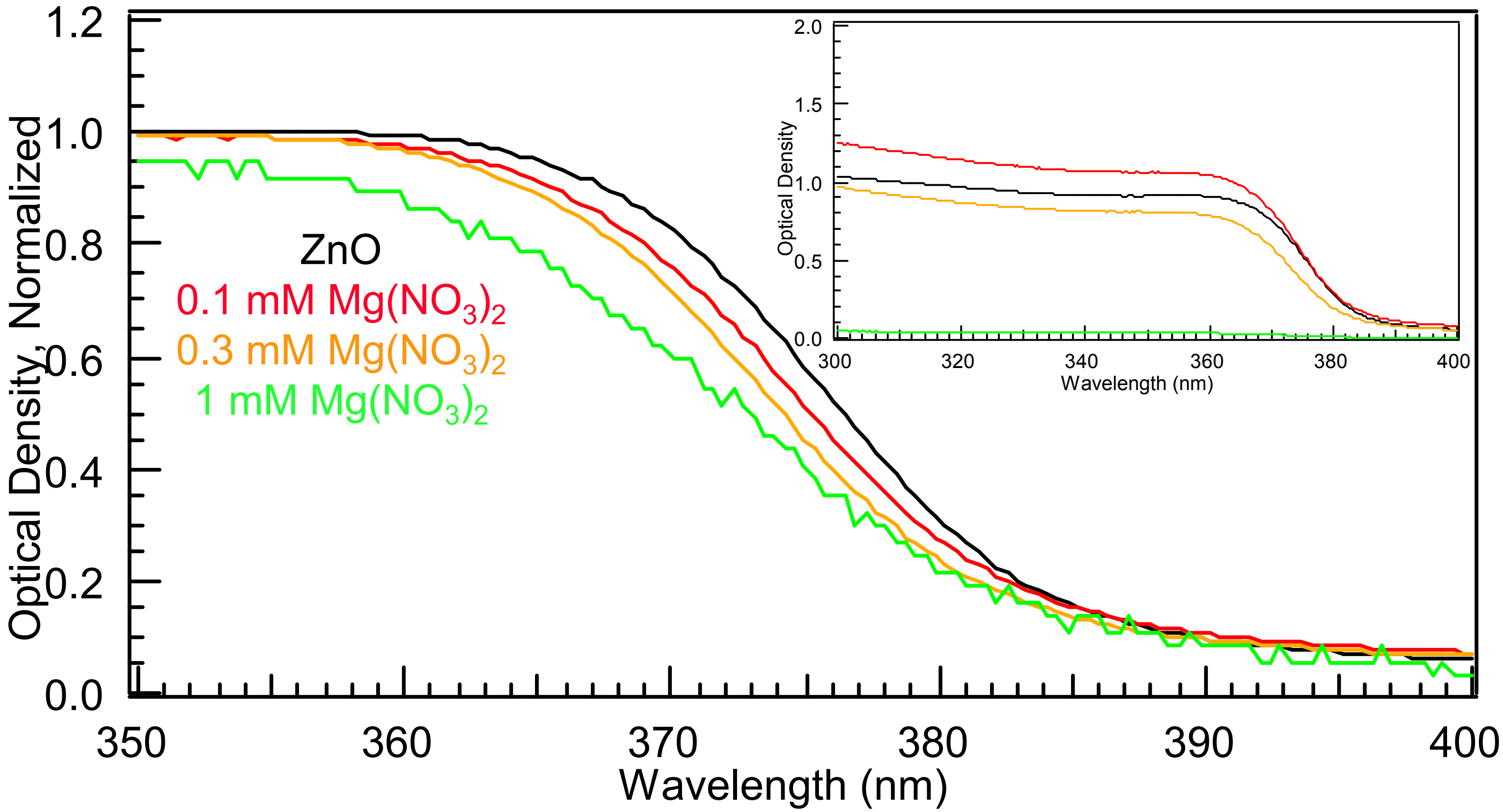
UV-vis of $Zn_{1-x}Mg_xO$ NRA



- Small monotonic blue shift in UV absorbance with $[Mg(NO_3)_2]$
- 0.3 mM $Mg(NO_3)_2$ --> 1% (atomic) Mg substitution
- Higher $[Mg(NO_3)_2]$ stops NRA growth

Conclusions and Future Work

- Growth solution pH affects ZnO NRA morphology and PL
  - Highly aligned NRAs due to seeding procedure
  - Nanorod number density ~ 10^{10} nanorods / cm^2
  - Neutral: close packed NRA, 45 nm diameter
  - Basic: ~ 10-20 nm spacing between rods, 35 nm diameter
  - Yellow-orange PL spectra, consistent with oxygen excess

- Addition of diaminopropane affects ZnO NRA morphology
  - DAP increases in ZnO length, diameter, and tapering
  - DAP chelates Zn^{2+} and regulates ZnO deposition

- $Zn_{1-x}Mg_xO$ NRA synthesized, but at low x values
  - Up to x = 0.01 Mg substitution achieved
  - Poor overlap in Mg and Zn solubilities as function of pH
  - Exploring nonaqueous hydrothermal method for high Mg subsitution

- Future work:
  - Determine effect of NRA packing on polymer infiltration
  - Synthesize $Zn_{1-x}Mg_xO$ NRAs with high Mg substitution
  - Compare PV devices made from different ZnO NRAs

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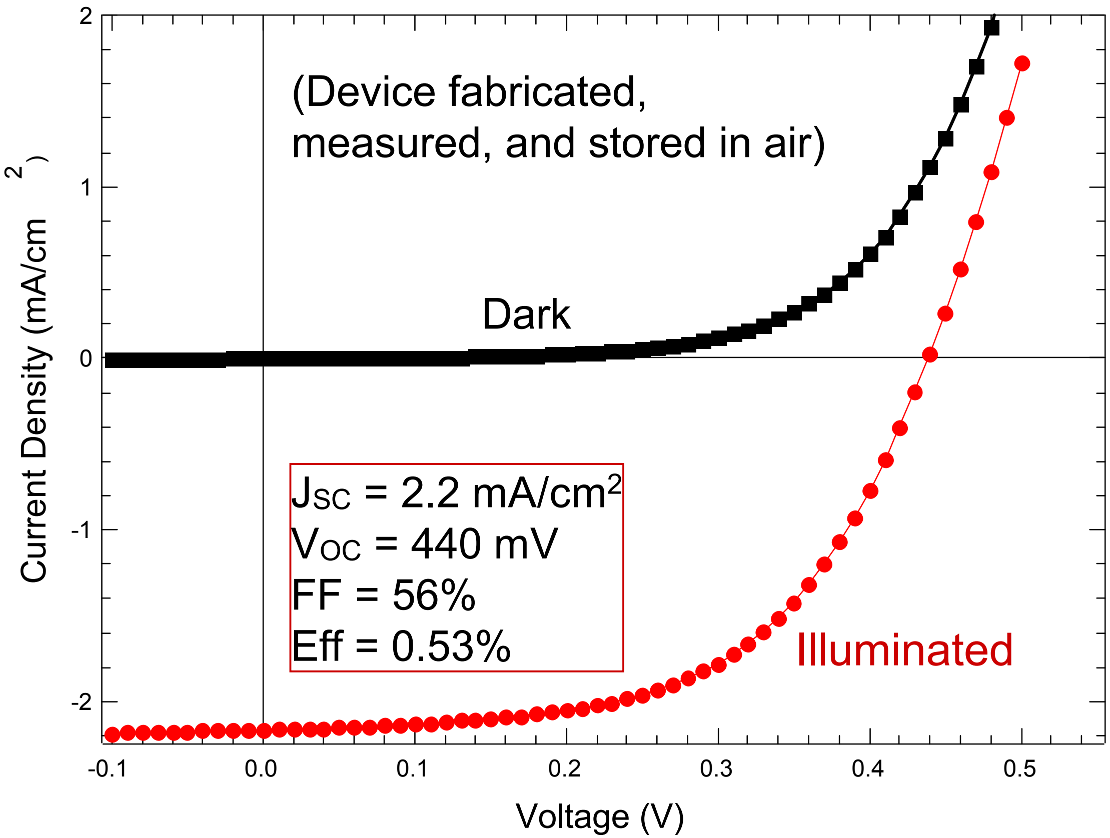
Outline

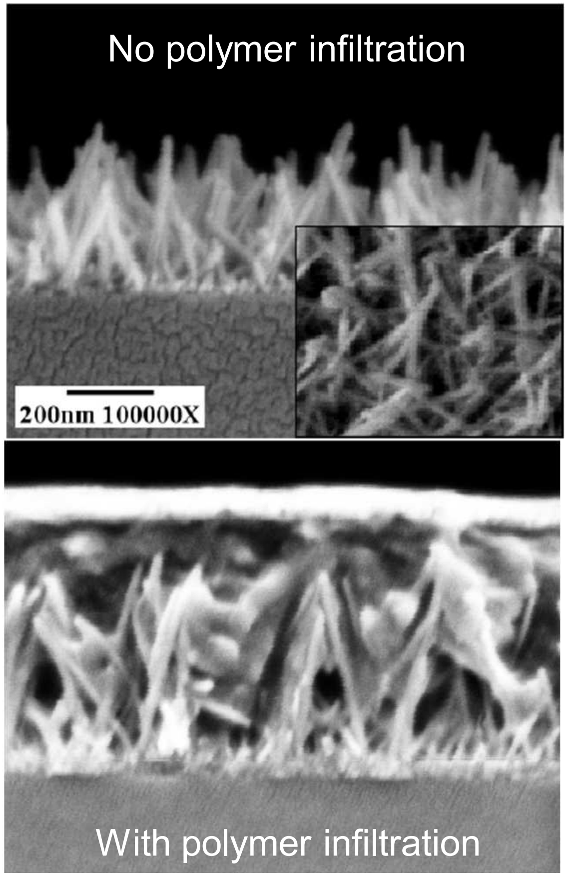
- Polymer/ZnO hybrid photovoltaic cells
  - Background and current progress
  - Opportunities for device optimization
- Effect of solution pH on ZnO NRA morphology
  - Growth rate/aspect ratio
  - NRA areal density
  - NRA PL
- Effect of amine additive on ZnO NRA morphology
- Synthesis of $Zn_{1-x}Mg_xO$ NRA
- Conclusions and Future Work

Polymer/ZnO Nanofiber PV Response

Best polymer/oxide nanorod device



ZnO nanofibers / P3HT



Disordered fiber array
Large spacing

D.C. Olson et al., *Thin Solid Films* **496**, 26 (2006)

Possible improvements:
- Increase interfacial area (nanorod density)
- Control inter-rod spacing
- Improve polymer infiltration

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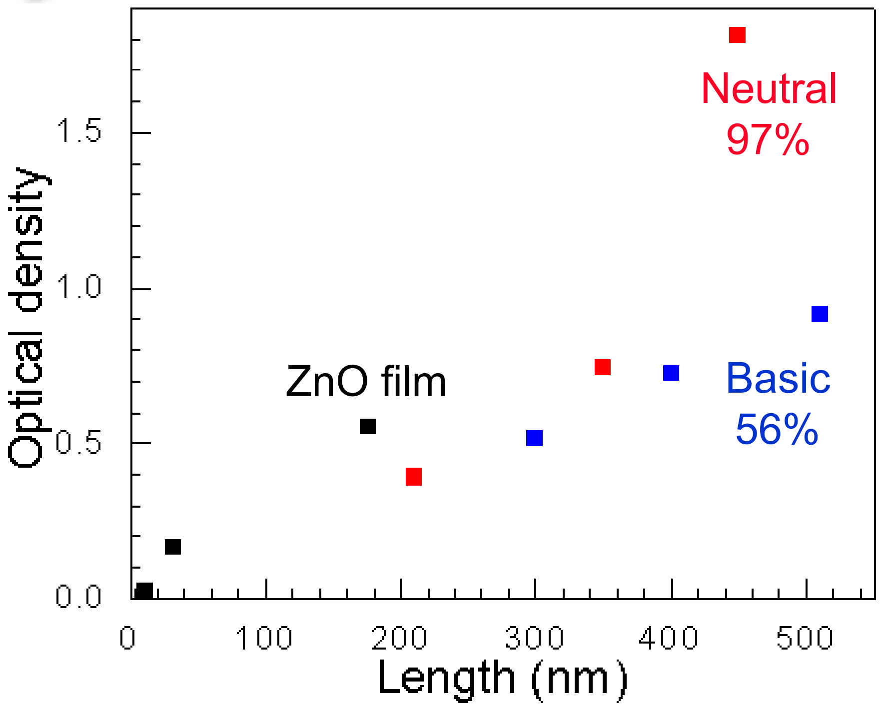
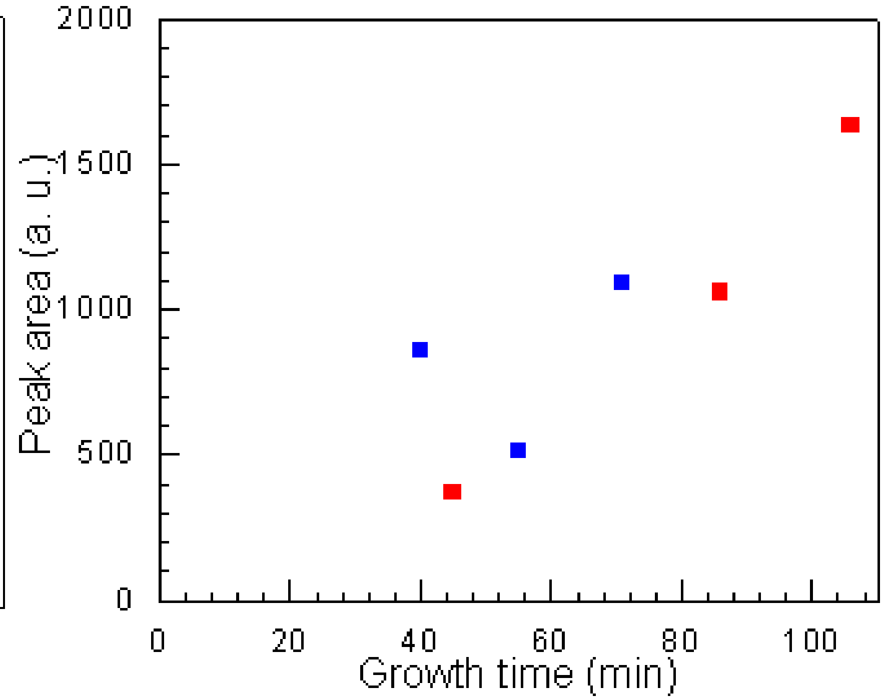
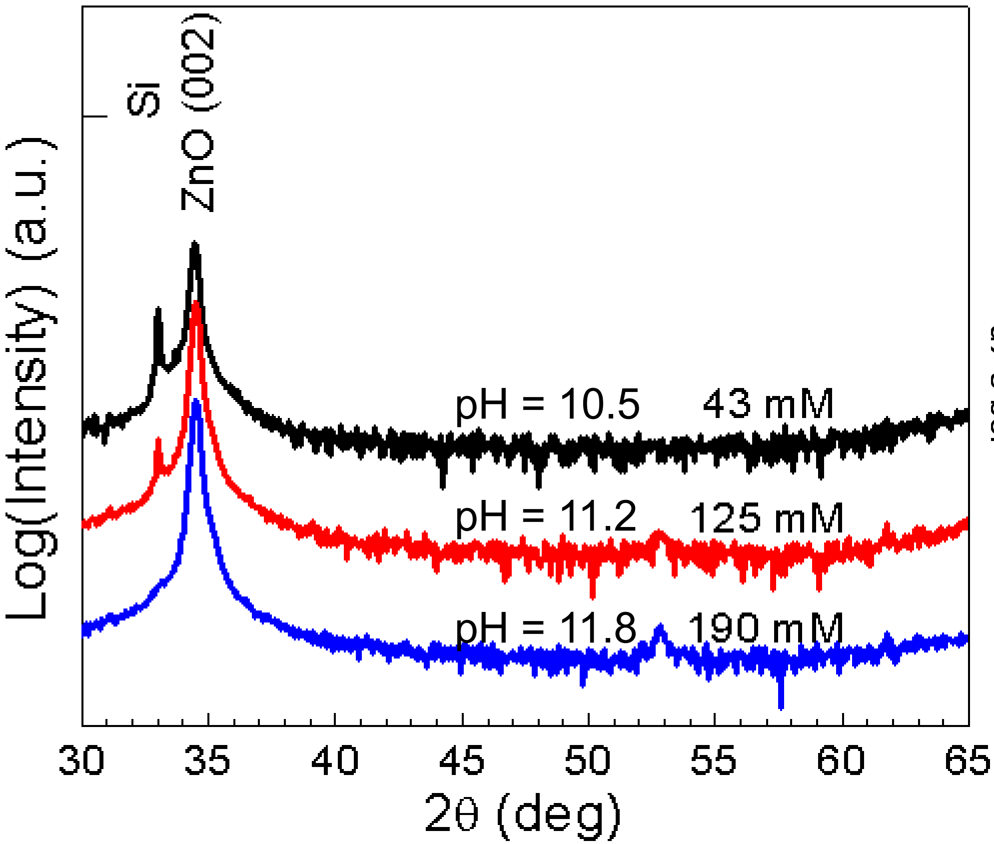
Areal Density of ZnO NRAs

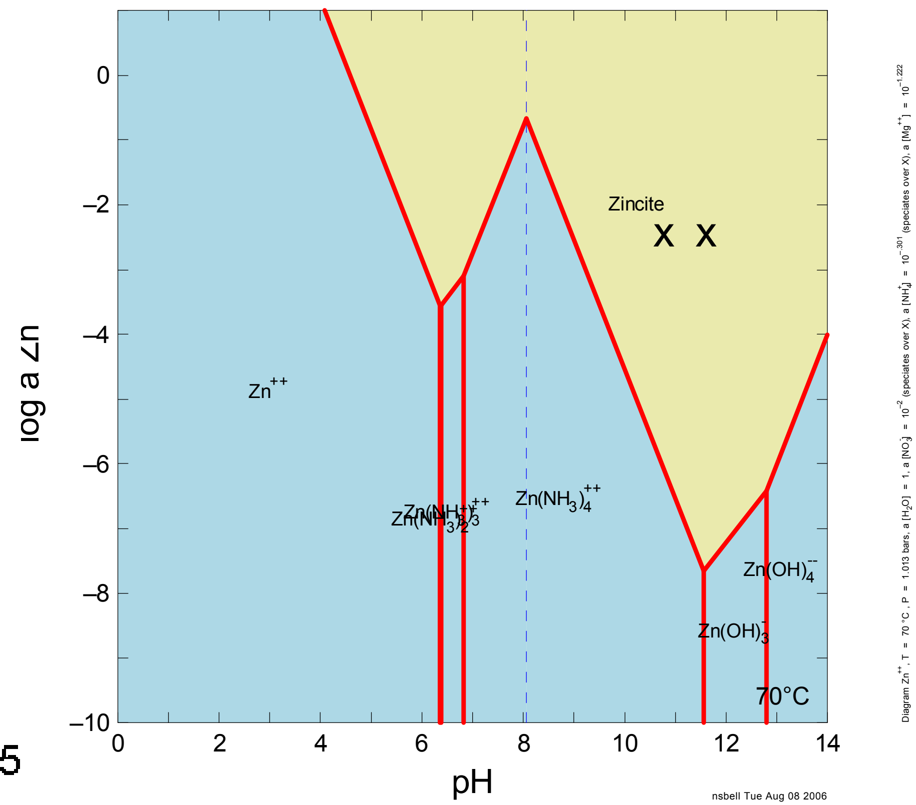




- Assume ZnO sol-gel film is 100% dense
- Relative density ratio ~ $(d_{basic}/d_{neutral})^2 = 0.6$
- Both NRAs have similar # density of rods

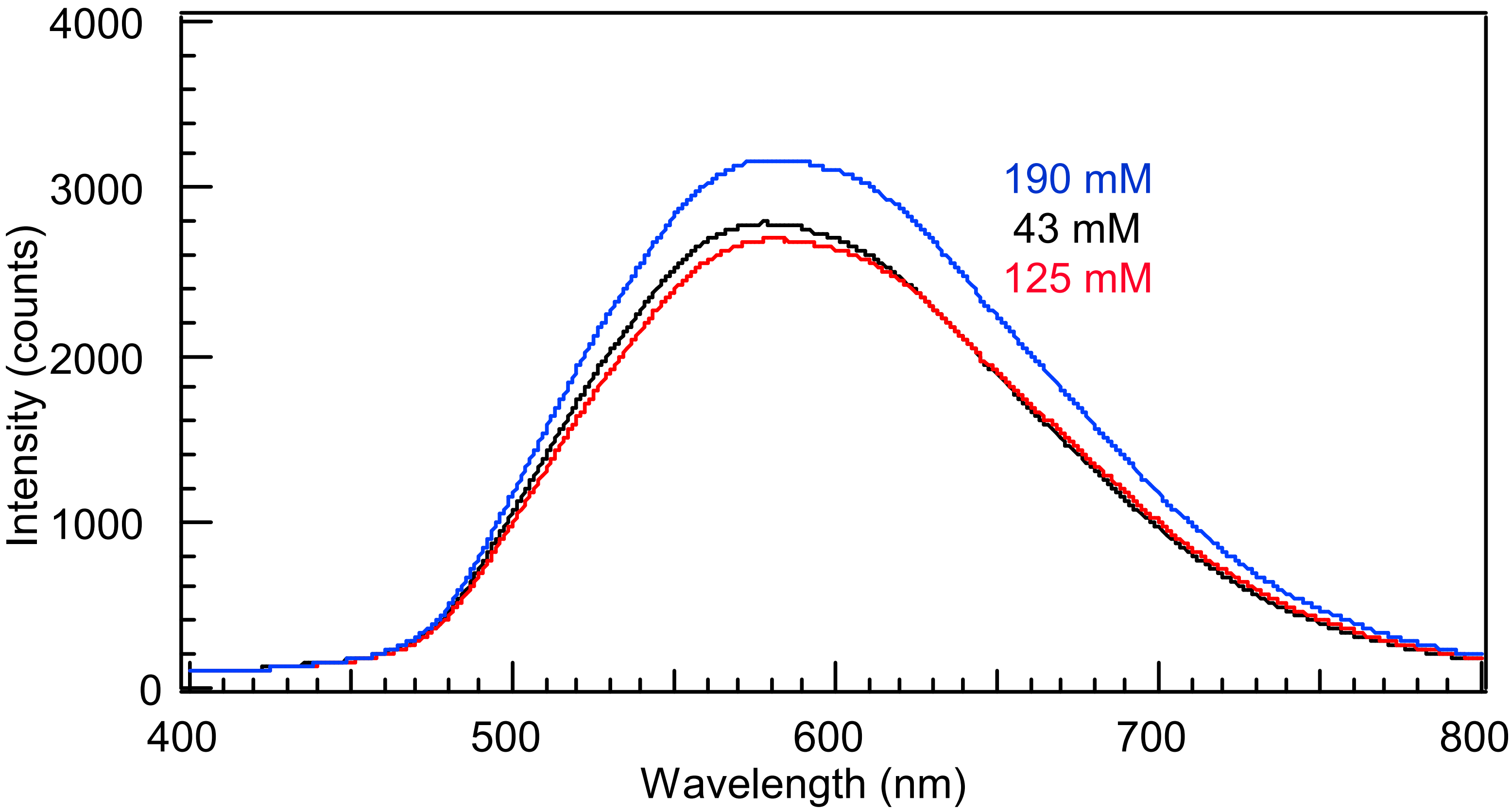
XRD and Speciation Diagram





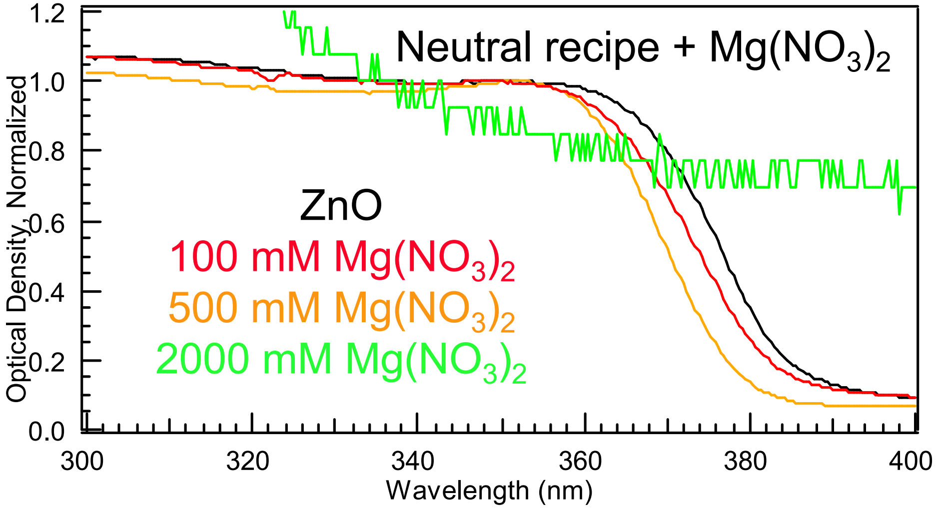
- Strong (002) peak intensity increases with [DAP]
- Aminated soluble species, decreased solubility with pH
- DAP increases growth rate by increasing pH and chelation

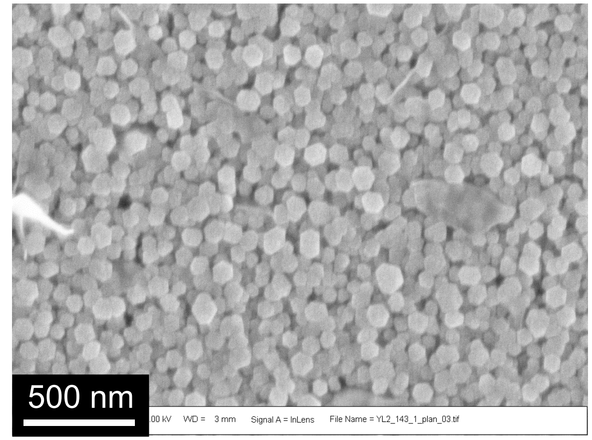
PL Spectra of ZnO NRA with DAP



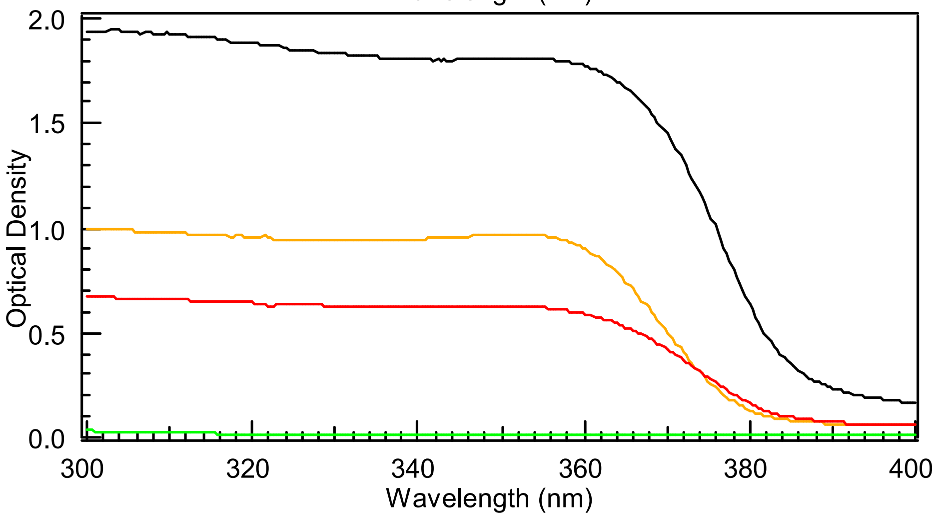
- Similar PL spectra (λ = 580 nm) as the neutral recipe ZnO
- No dependence of PL on growth rate
- Soluble species determines ZnO NRA PL?

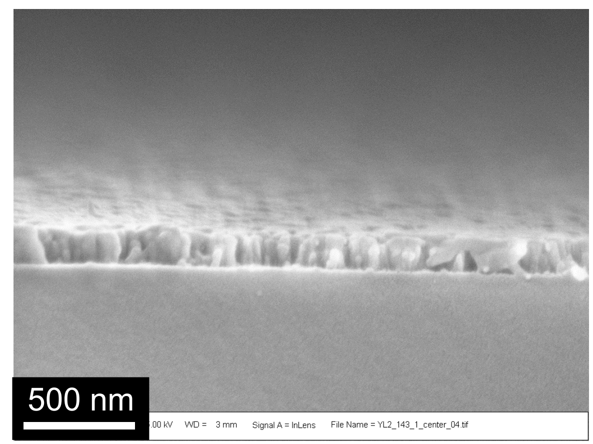
ZnMgO NRA Synthesis--Neutral





500 mM Mg(NO$_3$)$_2$, 100 min





- 500 mM Mg(NO$_3$)$_2$ --> 6 nm blueshift (3% Mg substitution)
- However, addition of Mg(NO$_3$)$_2$ results in short, fused NRA

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