SAND2008-4433C

Doping of Highly Oriented ZnO Nanorod Arrays via Aqueous Synthesis

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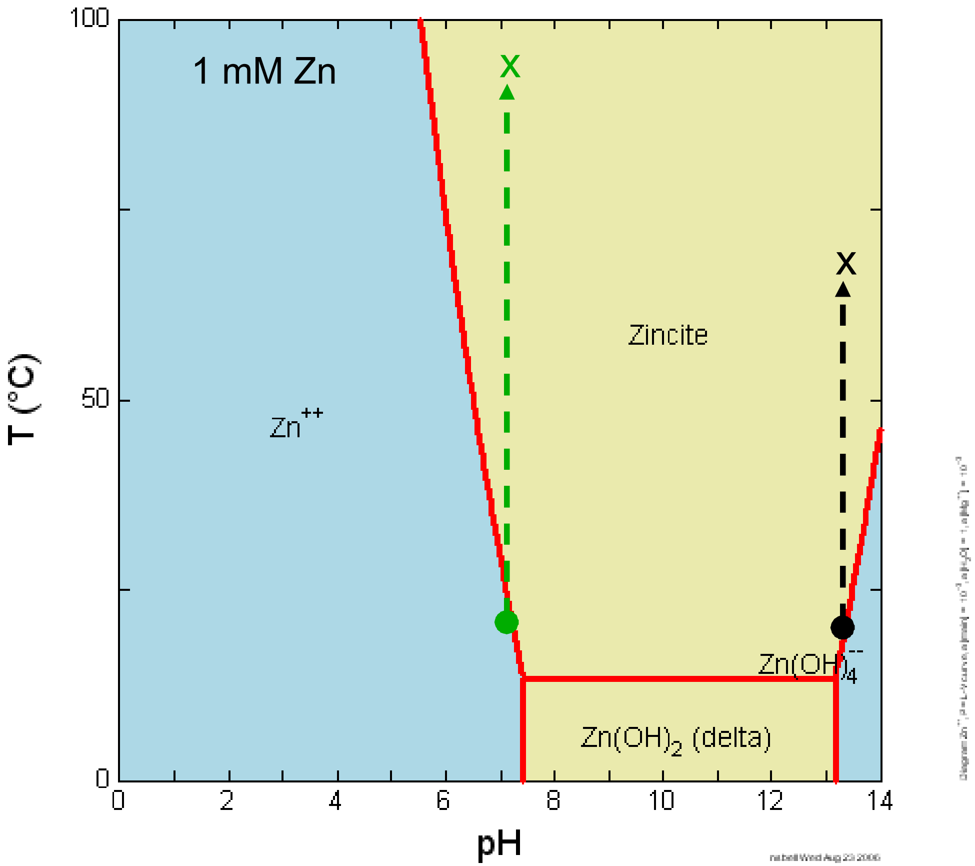
Acknowledgements: Bonnie McKenzie (SEM), Bill Wallace (XPS)

Funding: Laboratory Directed Research and Development program, SNL

EMC 2008
June 25, 2008

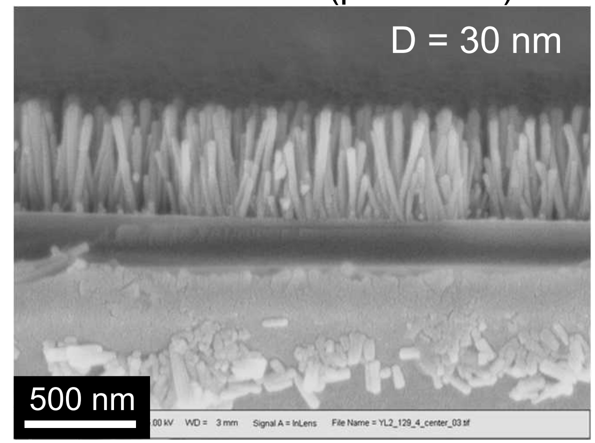
Zn Speciation Diagram



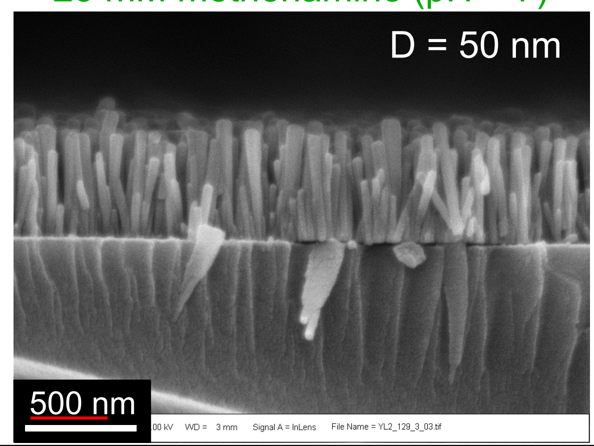
Y.-J. Lee et al., *J. Cryst. Growth*, **304**, 80 (2007)

Y.-J. Lee et al., *Cryst. Growth Design*, **8**, 2036 (2008)

90 mM NaOH (pH = 13.2)



25 mM methenamine (pH ~ 7)



- ZnO deposition caused by decreased solubility at high temperatures
- Nanorod length, diameter, aspect ratio, etc., depends on solution pH
- Morphology varies with concentration, temperature, time, stages, etc.

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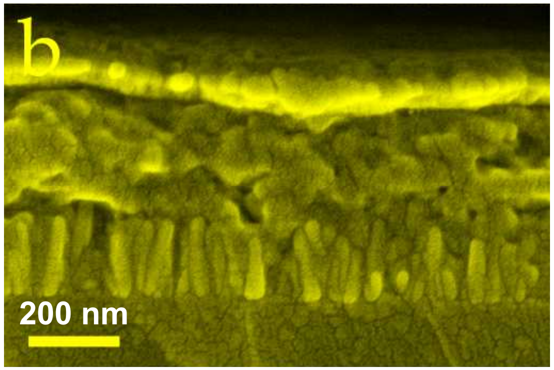
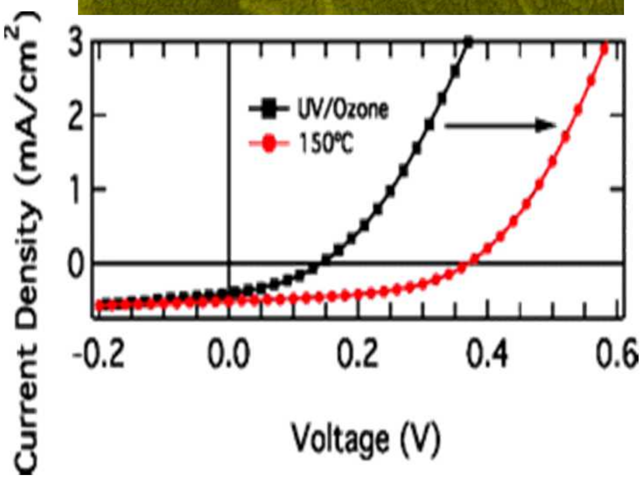
Applications for ZnO Nanorod Arrays

Hybrid photovoltaics



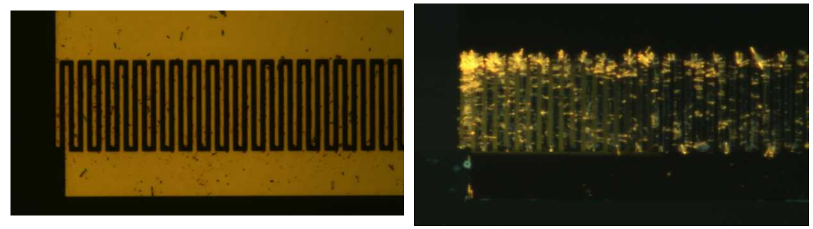


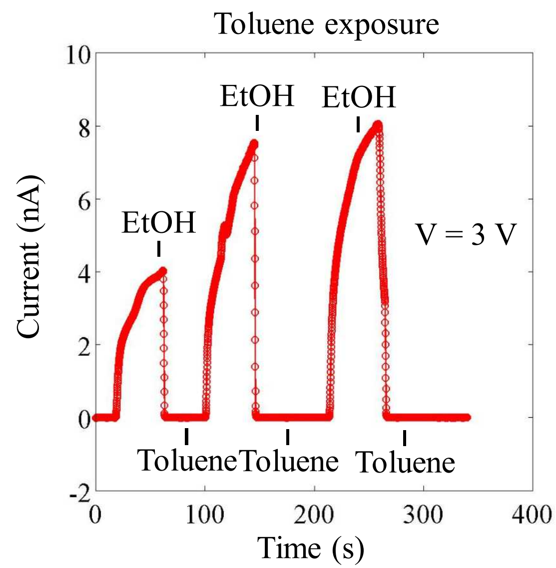
D. C. Olson et al., *J. Phys. Chem. C*, **111**, 16640 (2007)

D. C. Olson et al., *J. Phys. Chem. C*, in press

Nanorod sensors

ZnO nanorods on IDEs



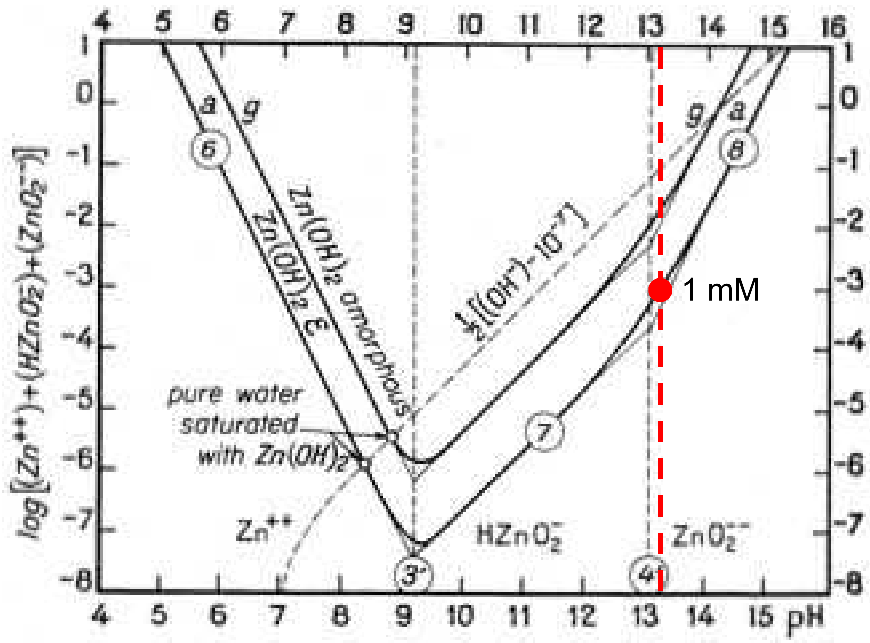


D. A. Scrymgeour (next talk)

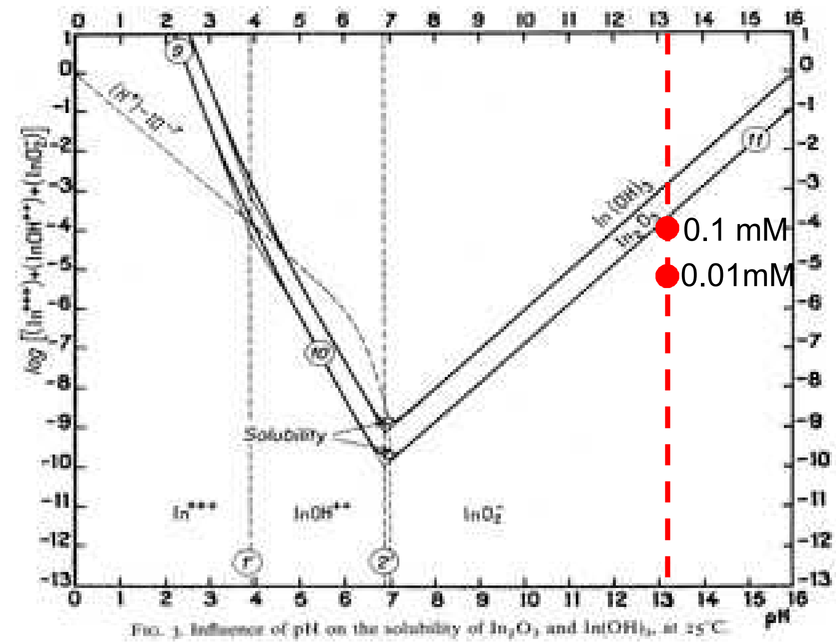
- Single crystalline, high interfacial area, controlled spacing
- Alter eletrical/optical properties → improved/new applications. Doping?

Codeposition with In

Zn speciation diagram at 25 °C



In speciation diagram at 25 °C



M. Pourbaix, *Atlas of Electrochemical Equilibria in Aqueous Solutions* (1966)

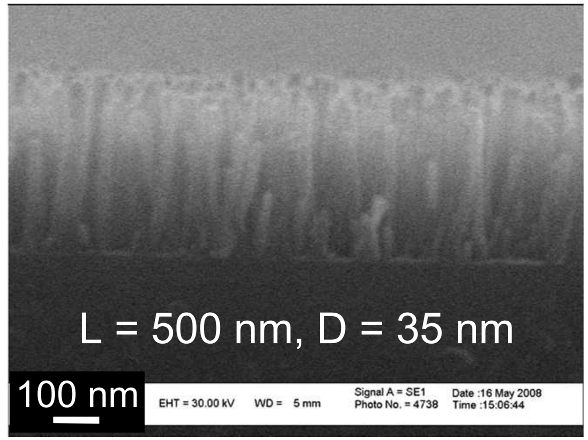
- At pH = 13.2, In ions are ~ 0.1 times as soluble as Zn ions
- Codeposit with 1 mM Zn and 0.1 mM or 0.01 mM In

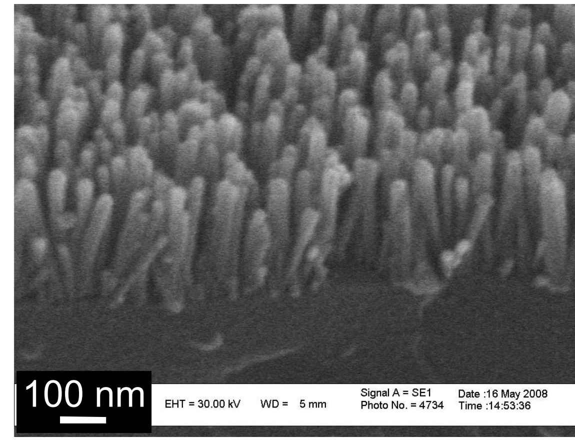
SEM of In Doped ZnO NRA

- 1 mM $Zn(NO_3)_2$, 90 mM NaOH, x mM $InCl_3$
- Grow at 70 °C for 40 min
- Nominal length = 500 nm

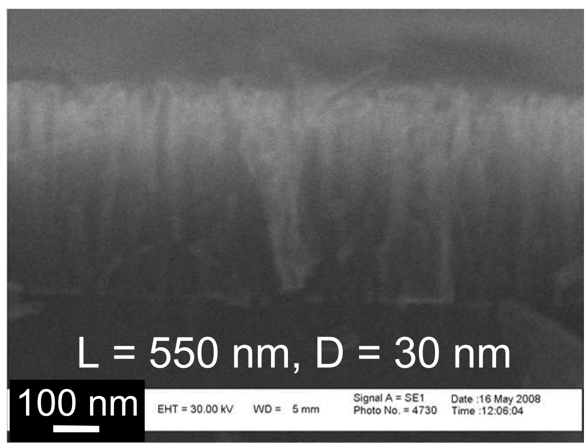
45° tilt

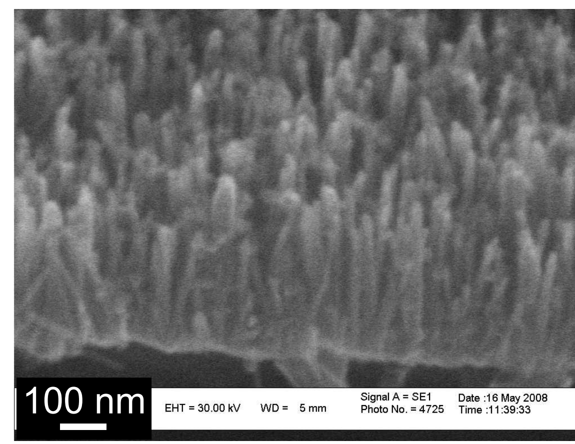
x = 0.01 mM





x = 0.1 mM





- Both In concentrations yield oriented nanorod arrays
- Similar nanorod dimensions for both In concentrations

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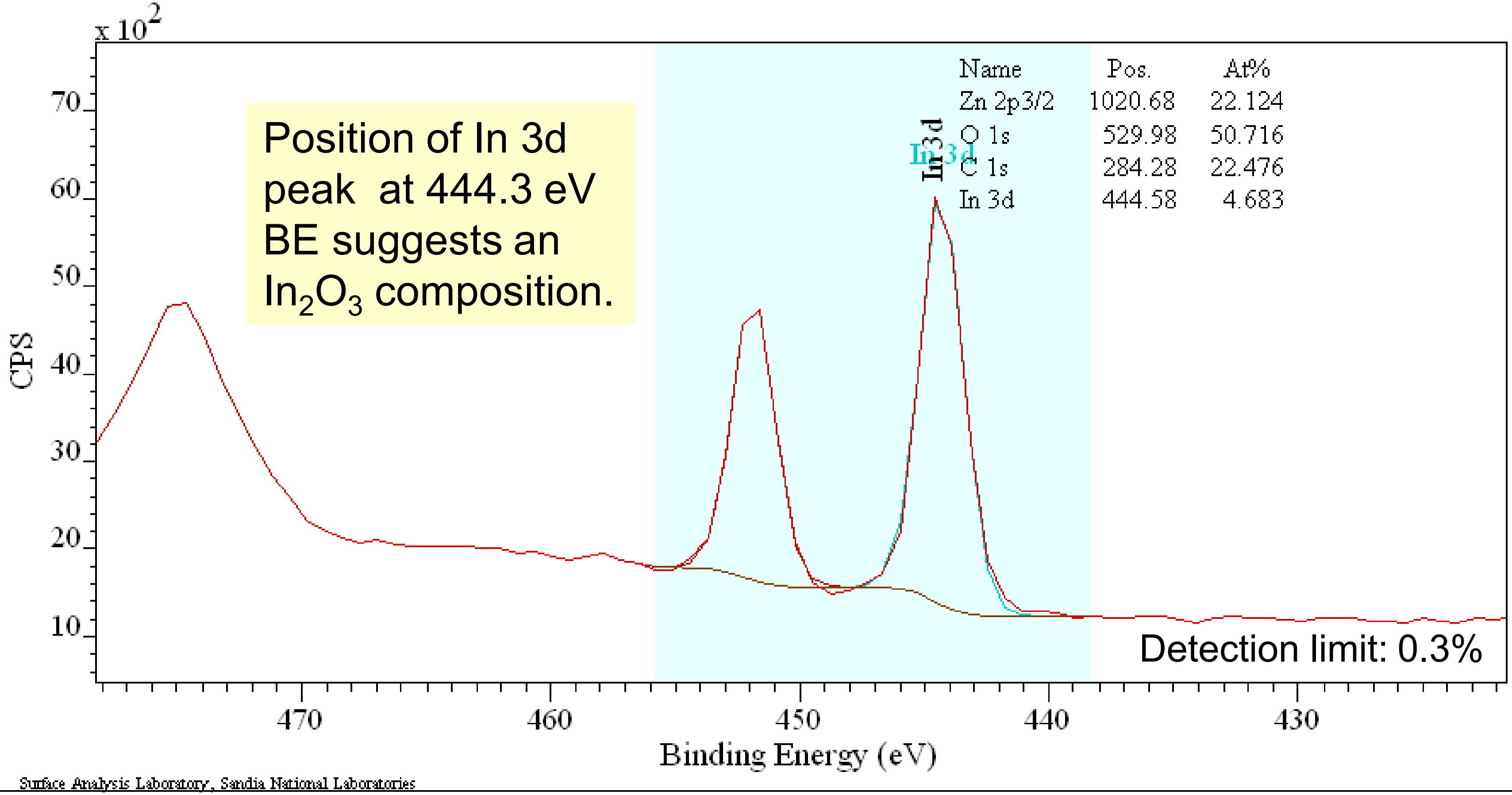
XPS of In Doped ZnO NRA

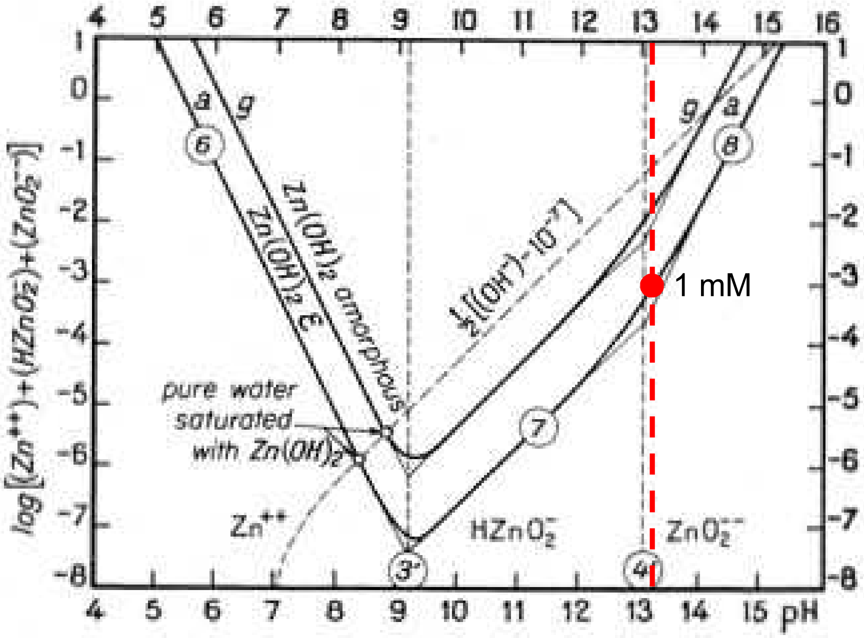
0.1 mM $InCl_3$



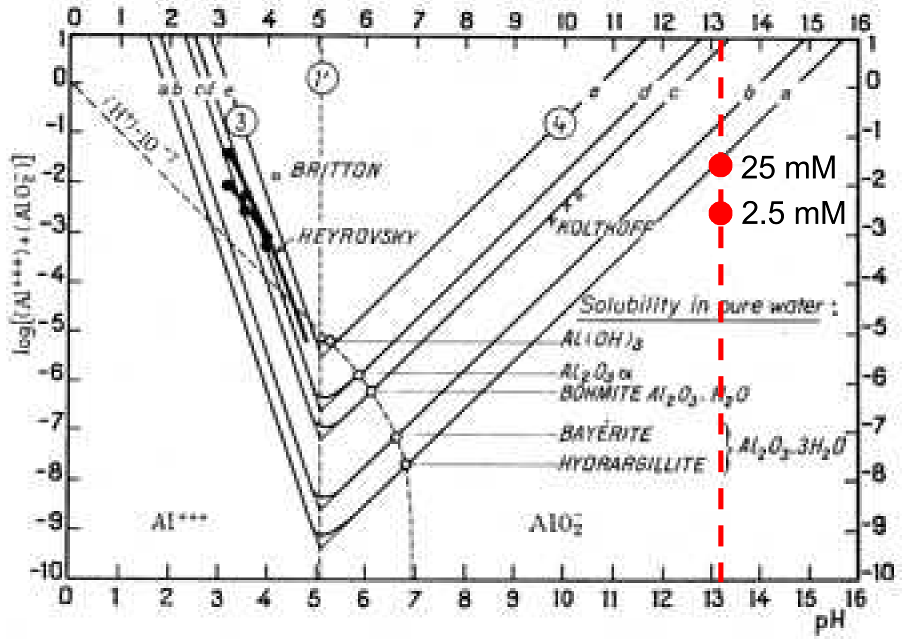
- 4.7% In in ZnO for 0.1 mM In solution, 1.4% In for 0.01 mM In solution
- In oxidation state (3+) suggests simple codeposition

Codeposition with Al

Zn speciation diagram at 25 °C



Al speciation diagram at 25 °C



M. Pourbaix, *Atlas of Electrochemical Equilibria in Aqueous Solutions* (1966)

- At pH = 13.2, Al ions is ~ 25 times as soluble as Zn ions
- Codeposit with 1 mM Zn and 25 mM or 2.5 mM Al

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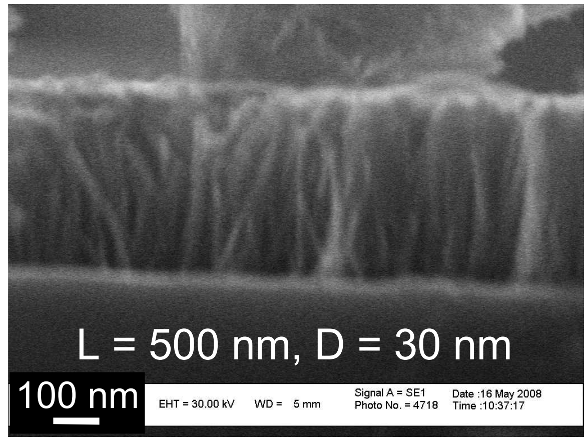
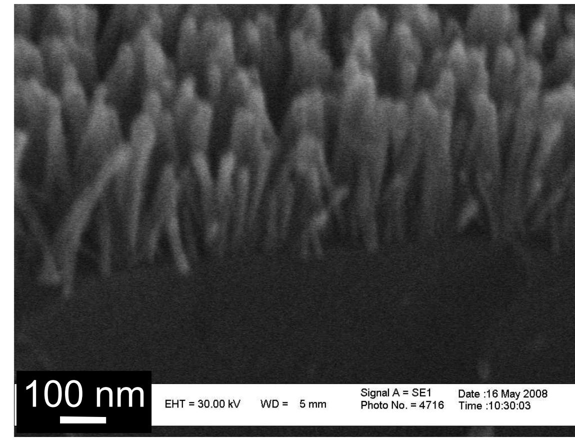
SEM of Al Doped ZnO NRA

- 1 mM $Zn(NO_3)_2$, (90+4x) mM NaOH, x mM $AlCl_3$
- Grow at 70 °C for 40 min
- Nominal length = 500 nm

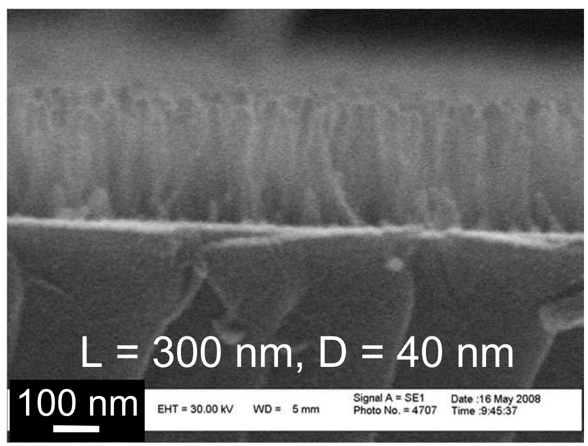
45° tilt

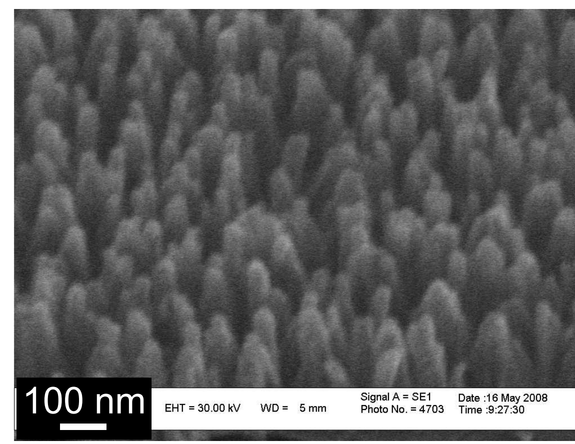
x = 2.5 mM





x = 25 mM





- Additional NaOH needed to keep pH = 13.2, suggests $Al(OH)_4^-$ as ion
- 25 mM Al results in shorter nanorods with larger diameters

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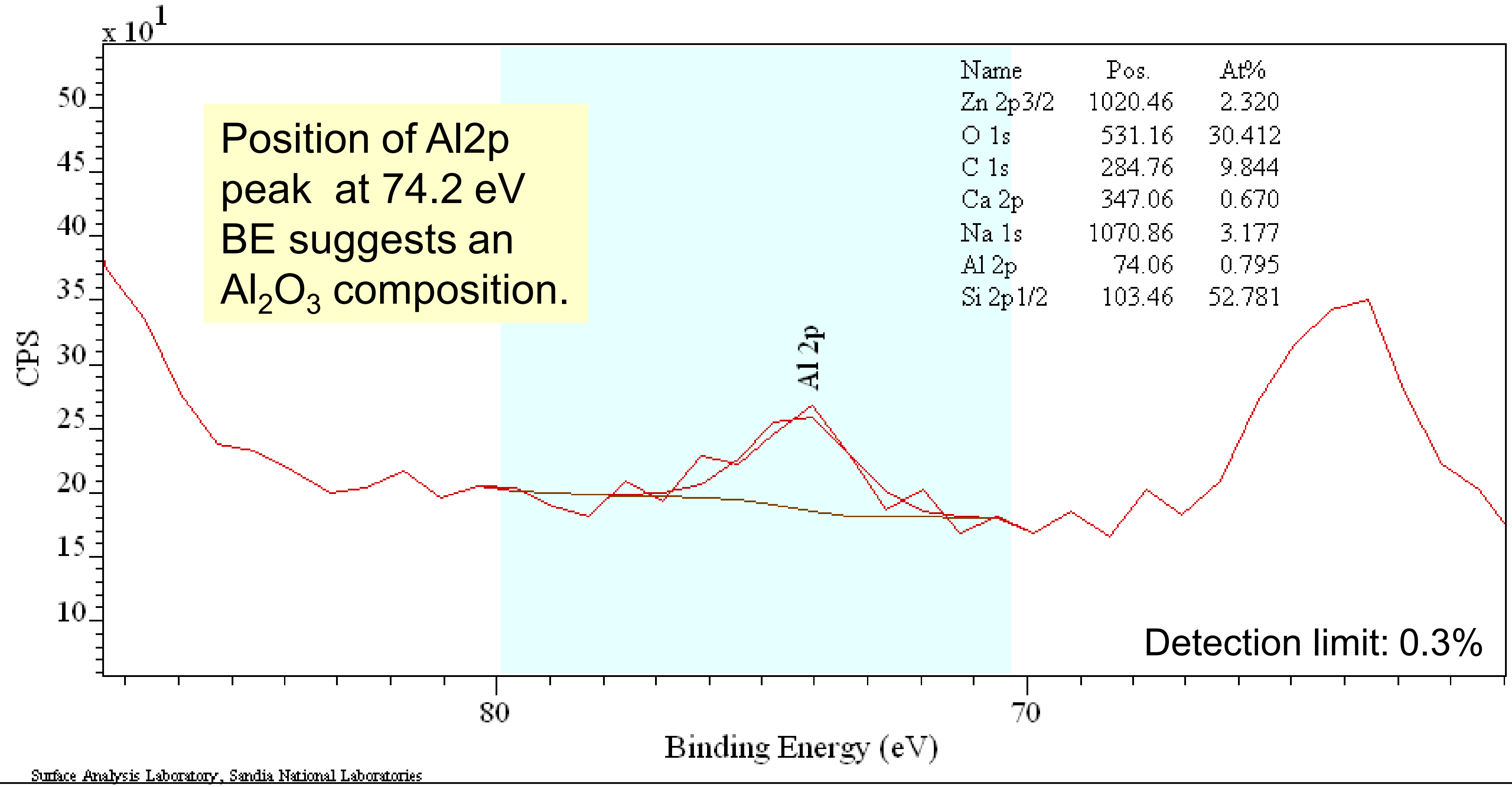
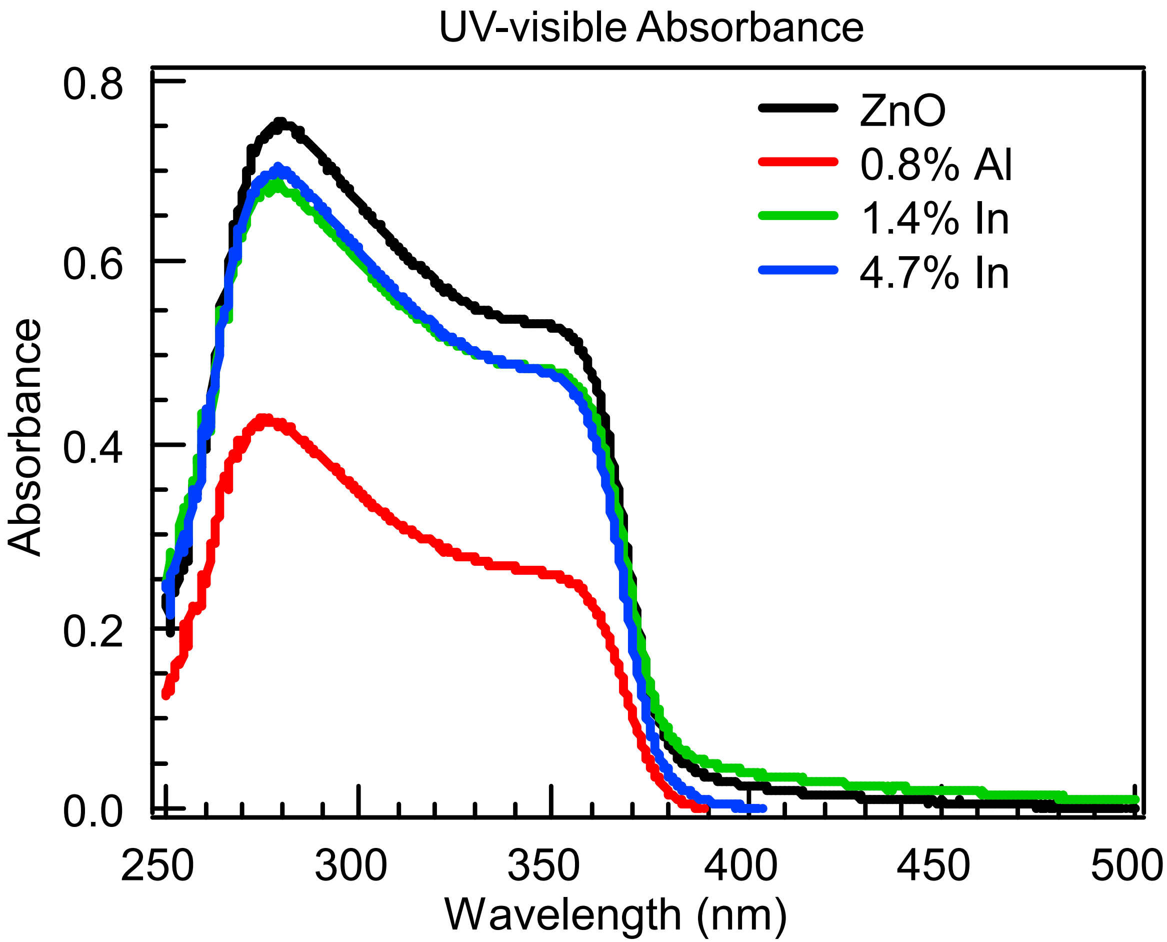
XPS of Al Doped ZnO NRA

25 mM $AlCl_3$



- 0.8% Al in ZnO for 25 mM Al solution, no change in oxidation state
- Al content in ZnO Below detection limit for 2.5 mM Al solution

Optical Response of Al/In Doped ZnO



- Optical band gap not shifted with addition of Al or In
- Significantly lower absorbance for 0.8% Al NRA, corroborating SEM result

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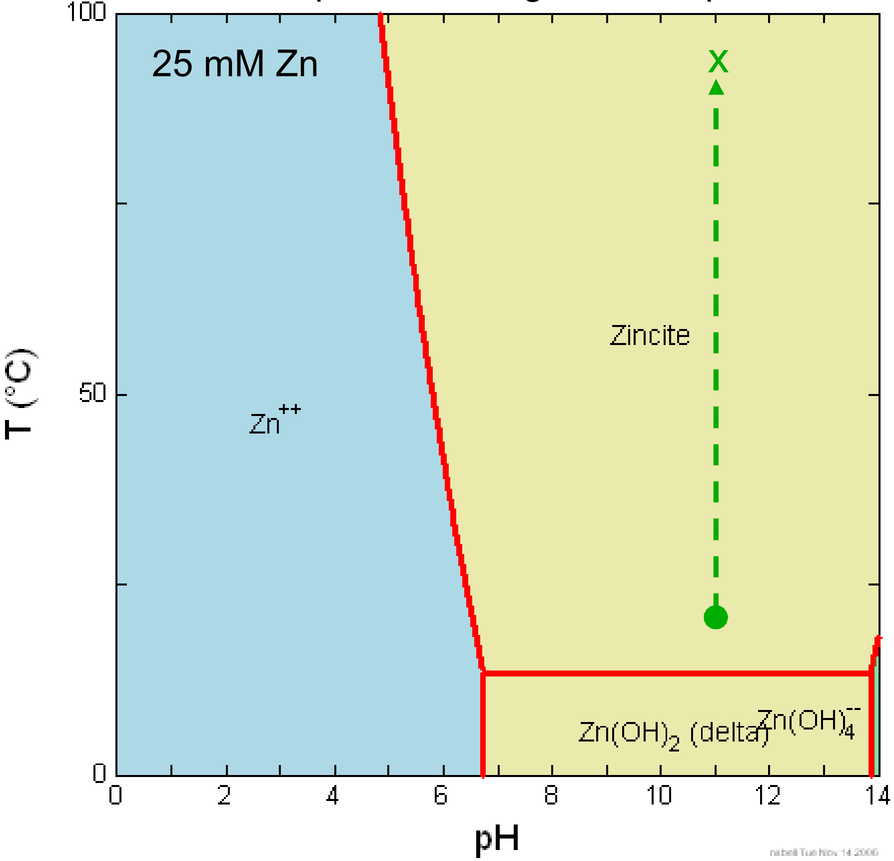
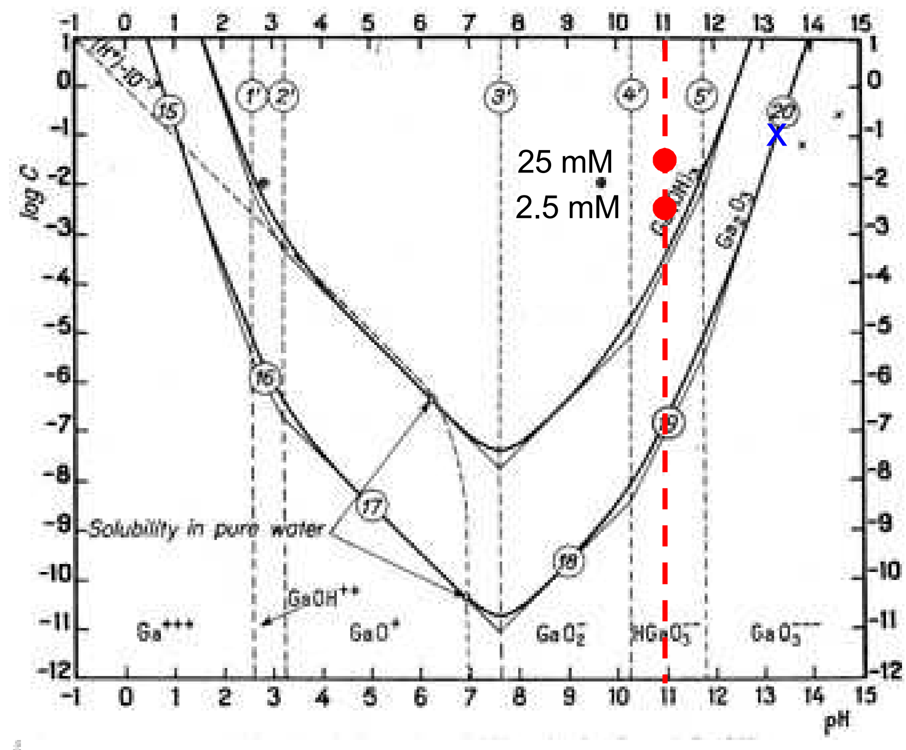
Codeposition with Ga and Stabilizer

Zn speciation diagram vs T, pH



Y.-J. Lee et al., *Cryst. Growth Design*, **8**, 2036 (2008)

Ga speciation diagram at 25 °C



M. Pourbaix, *Atlas of Electrochemical Equilibria in Aqueous Solutions* (1966)

- 1,3-diaminopropane (DAP) allows Zn, Ga to dissolve at pH = 11
- However, interactions between DAP and metal ions increases complexity

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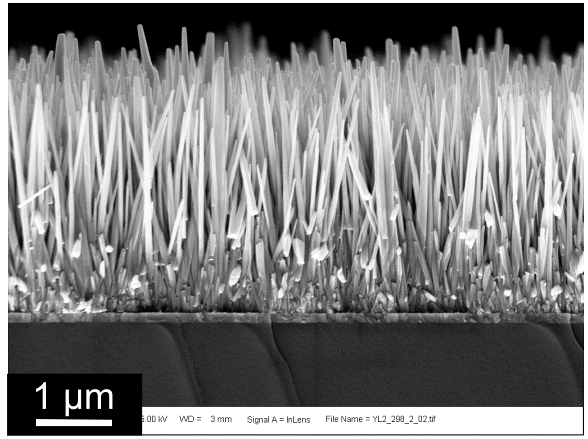
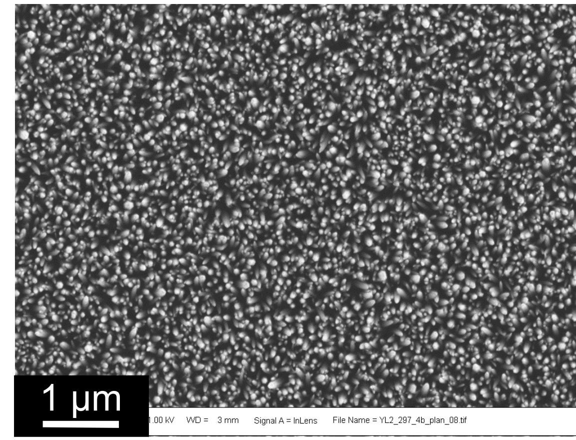
SEM of Ga Doped ZnO NRA

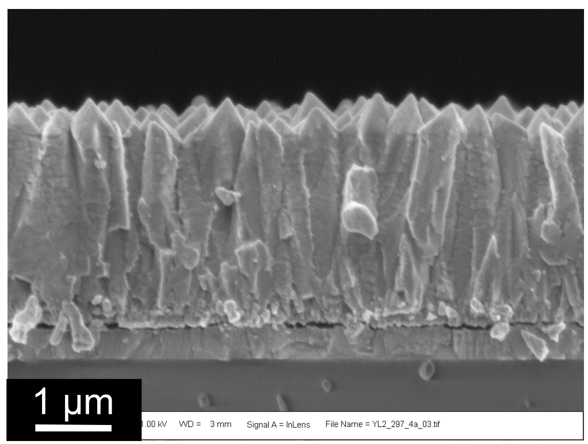
- 25 mM $Zn(NO_3)_2$, 25 mM methenamine, 190 mM 1,3-diaminopropane, x mM $Ga(NO_3)_3$
- Grow at 92.5 °C for 1 hr
- Nominal length = 2.5 μm

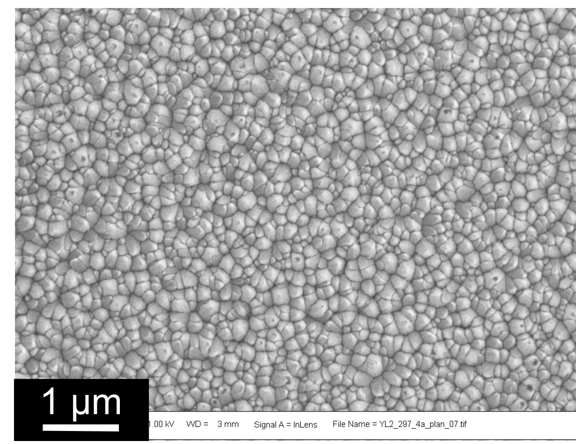
x = 2.5 mM





x = 25 mM





- At 25 mM Ga, NRA length decreases slightly and becomes fused
- Chelating agent has high affinity for Zn, limiting usefulness of technique

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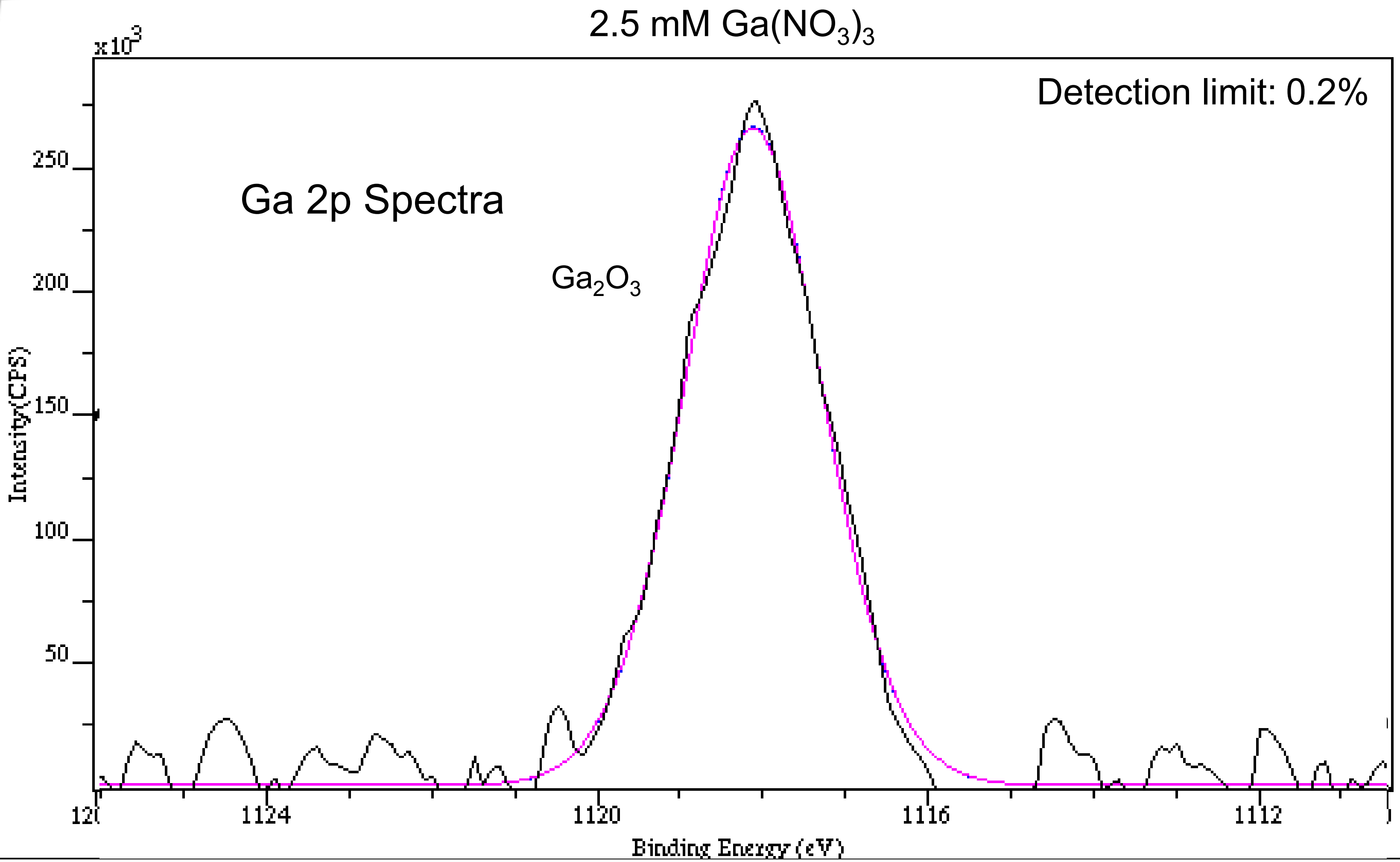
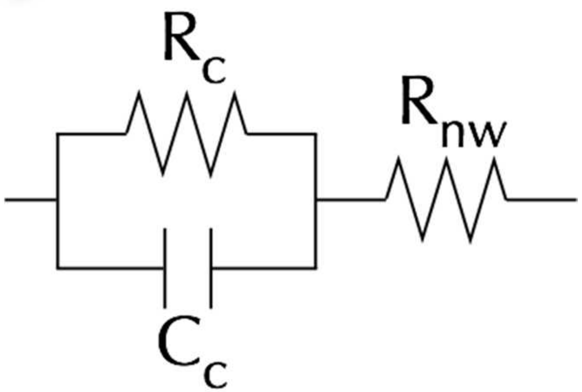
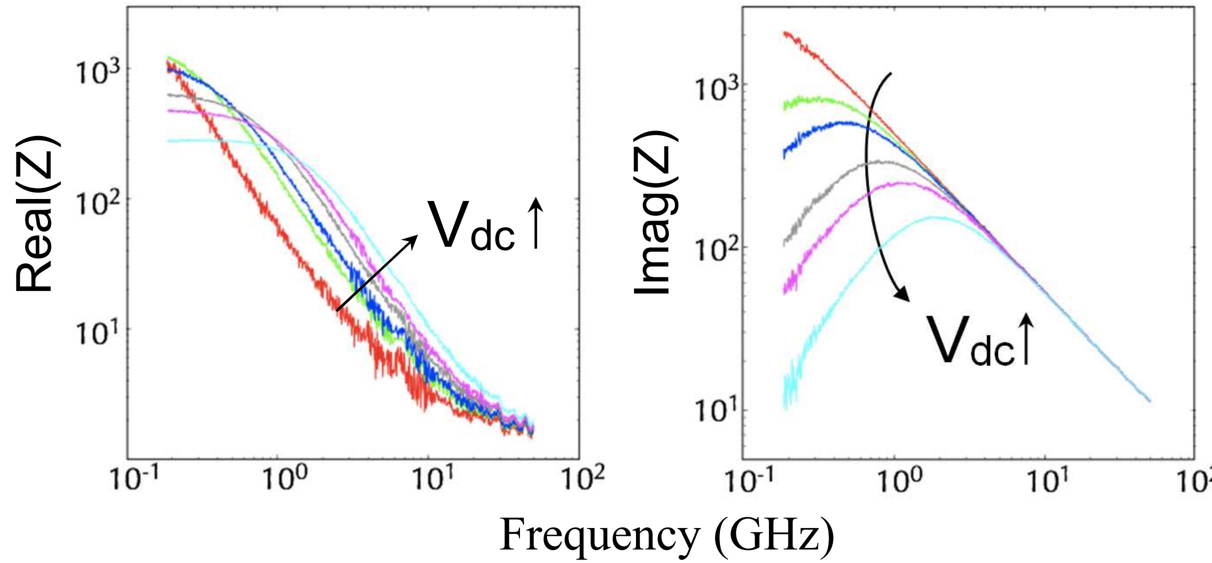
XPS of Ga Doped ZnO NRA

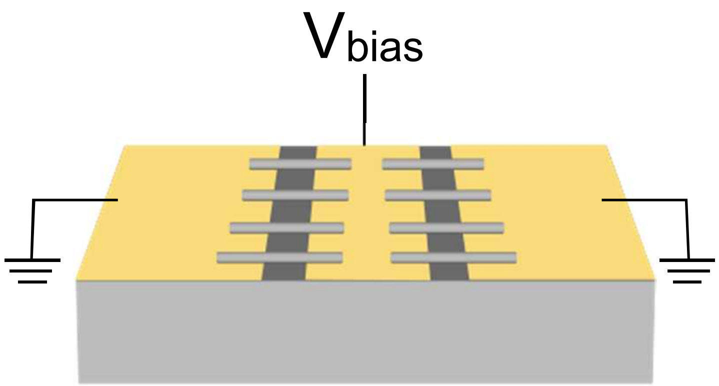


- 0.3% Ga in ZnO for 2.5 mM Ga solution
- Again, Ga oxidation state (3+) suggests simple codeposition

Resistance of Ga Doped ZnO NRA







	C_c ($x10^{-16}$ F)	R_{nw} (Ω)
ZnO - DAP	1.65	1761.2
Ga doped ZnO	1.61	980.0

- 40% decrease in resistance compared to undoped ZnO nanorods
- Implies uniform incorporation of Ga as n-type dopant

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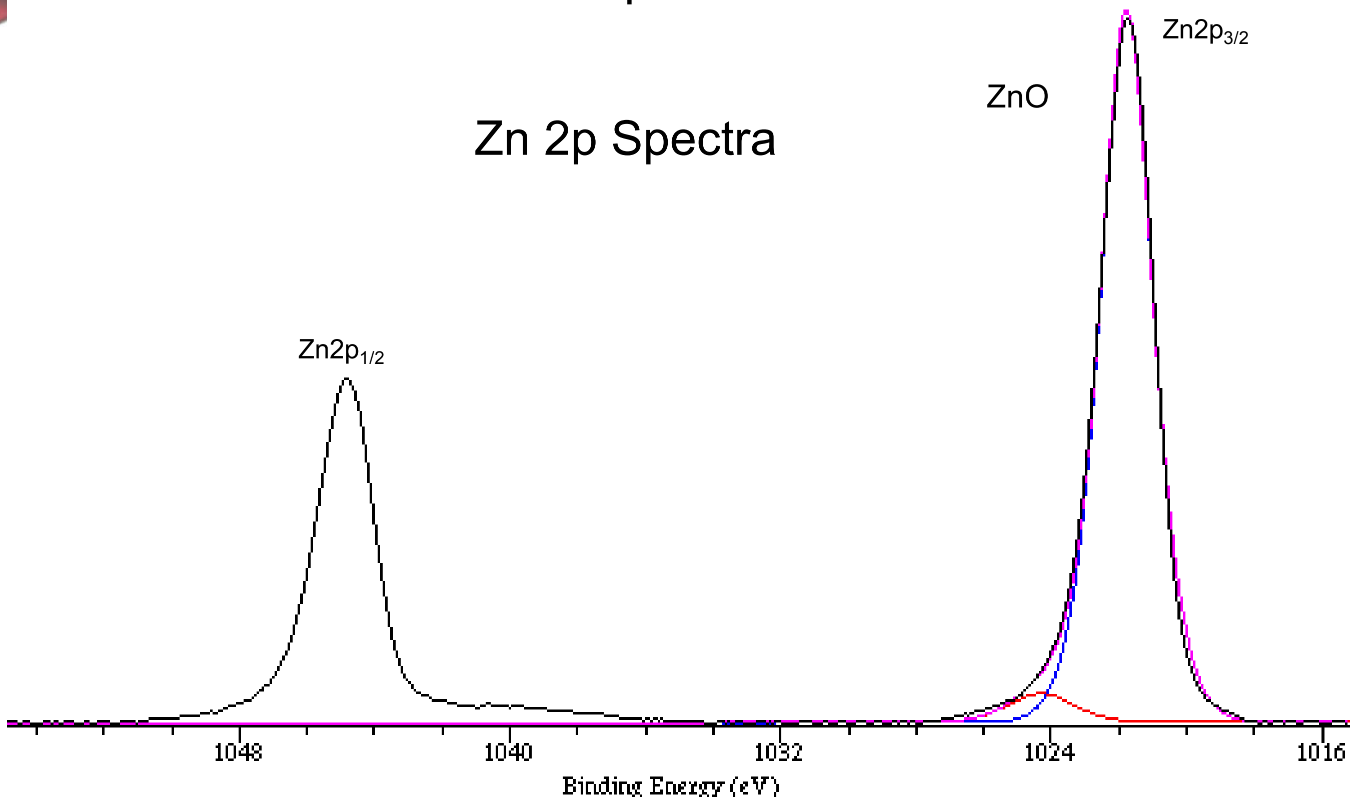
Conclusions and Future Work

- Aqueous codeposition utilized to create ZnO NRAs with high levels of dopant incorporation
  - 4.7% In in ZnO from saturated In solution (lower solubility than Zn)
  - 0.8% Al in ZnO from saturated Al solution (higher solubility than Zn)
  - 0.3% Ga in ZnO from solution with DAP chelating agent
- Properties of doped ZnO NRAs examined
  - Large solubility mismatch can adversely affect NRA growth (sat Al)
  - Impendance measurement suggests Ga is n-type dopant
  - UV-vis spectroscopy suggests no change in optical band gap
- Future work
  - Measure electrical properties of In and Al doped ZnO NRA
  - Study carrier compensation to reduce n-type response of ZnO NRA
  - Explore doping to shift optical response of ZnO NRA
  - Fabricate and test PV and sensor devices

Ga-doped

Zn 2p Spectra

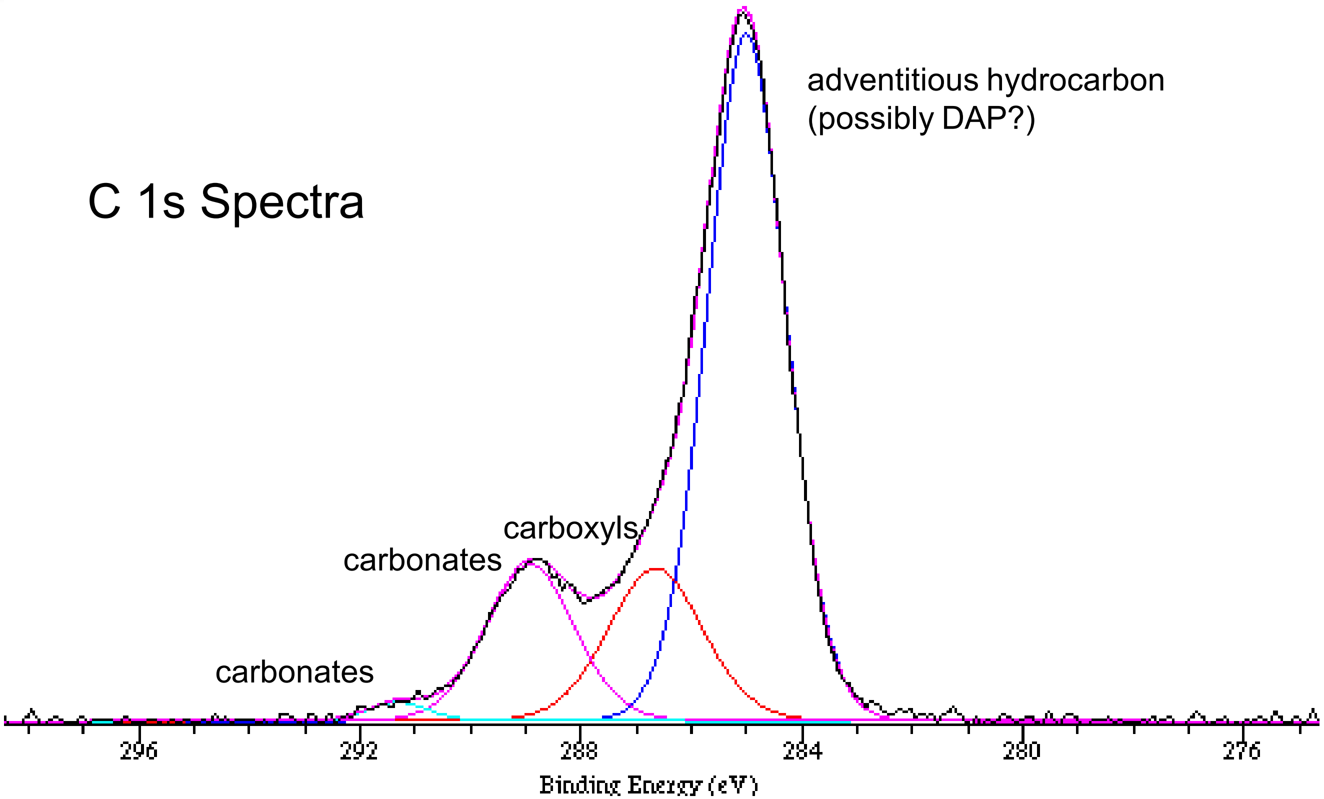


Elemental Atomic Percent
Zn 40%

Relative to Total Concentration
ZnO 40%

Ga-doped

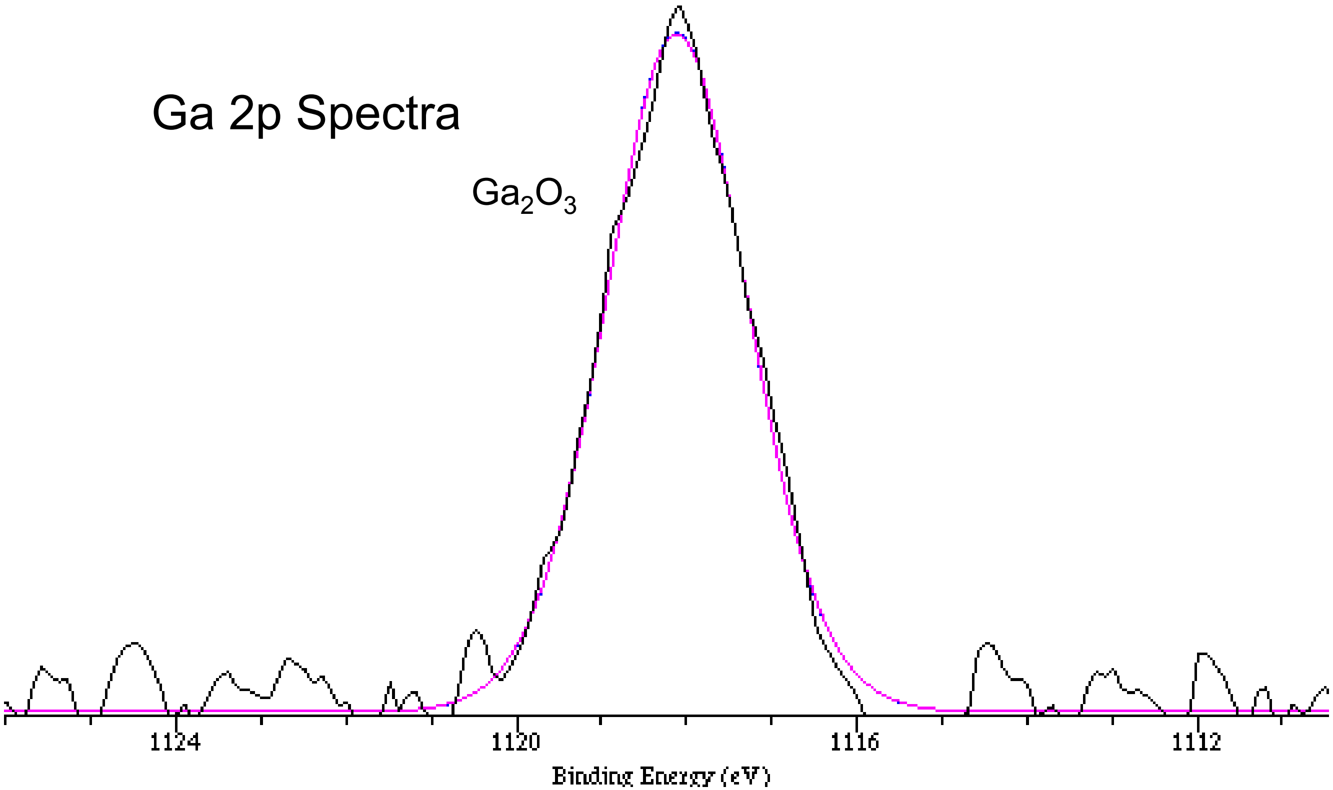
C 1s Spectra



Elemental Atomic Percent	Relative to Total Concentration	
C 17%	adventitious hydrocarbon	11%
	carbonates	3%
	carboxyls	3%

Ga-doped

Ga 2p Spectra

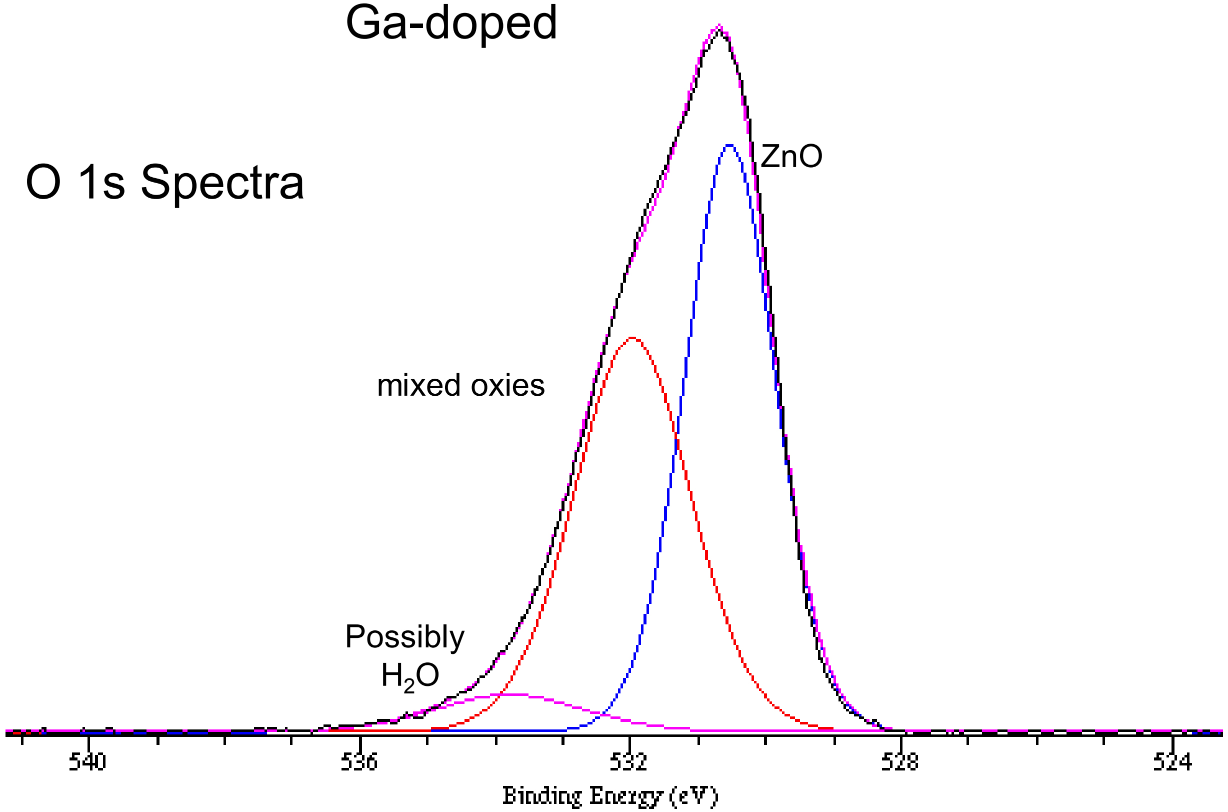


Elemental Atomic Percent — Relative to Total Concentration

Elemental Atomic Percent	Relative to Total Concentration
Ga 0.3%	Ga_2O_3 0.3%

Ga-doped

O 1s Spectra



Elemental Atomic Percent	Relative to Total Concentration	
O 42%	ZnO	21%
	mixed oxides	18%
	possibly H_2O	2%