Fabrication of ZnO Nanowire Arrays for Hybrid Photovoltaic Applications

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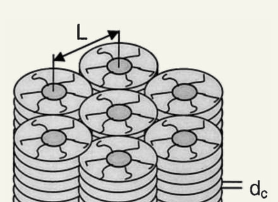
Goals and Summary

Primary goals:
- Controlled fabrication of uniform ZnO nanowire arrays on Si substrates via chemical vapor deposition with vapor-liquid-solid (VLS) mechanism
- Optimization of growth parameters
- Fabrication of hybrid photovoltaic cells using ZnO and smectic octylcyanobiphenyl (8CB) liquid crystals

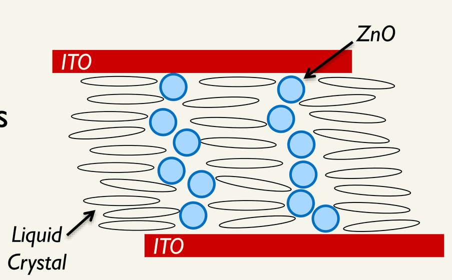
Summary of work:
- Achieved reproducible growth of ZnO nanowire arrays on Si in horizontal tube furnace
- Determined effect of various growth parameters on resulting arrays
- Observed enhanced optical absorption when nanowires and liquid crystal are combined
- Nanowires seem to grow by non-VLS mechanism

Motivation

- Combination of inorganic nanostructures and organic material can improve absorption and mechanical properties
  - Dye-sensitized solar cells [1]
  - Flexible ZnO/P3HT bulk heterojunctions [2]

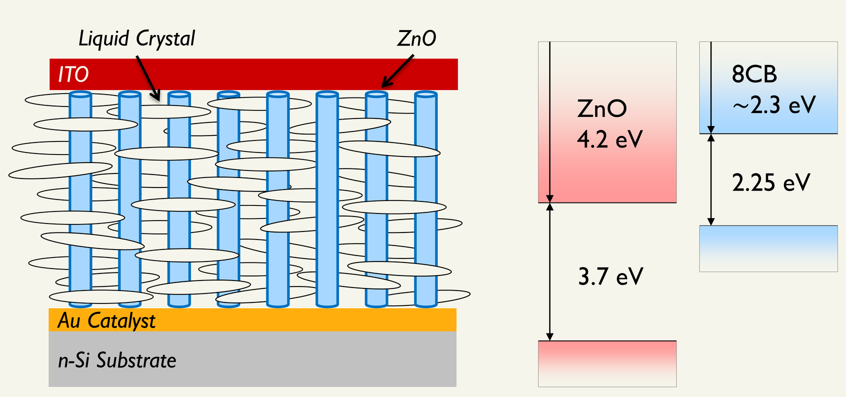


- Liquid crystal photovoltaics can self-organize, enhancing charge transfer along axis of orientation [3]



- Incorporating ZnO nanoparticles enhances order of liquid crystal, greatly improving hole mobility [4]
- **Could a continuous inorganic pathway (nanowires) have the same effect?**
  - Enhanced hole conduction from liquid crystals
  - Enhanced electron conduction in nanowires
- **Can we control the morphology of ZnO nanowire arrays?**

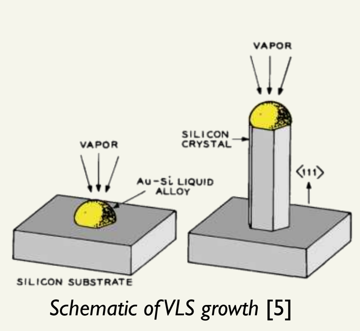
Hybrid Photovoltaic Design



- Use smectic octylcyanobiphenol (8CB) to investigate ordering between liquid crystal and nanowires
  - Compare to ordering with nanoparticles
- Expected band structure
  - ZnO: electron conductor
  - 8CB: hole conductor

Methods & Experimental Parameters

- Vapor-liquid-solid nanowire growth method [5]
  - Chemical vapor deposition technique
  - Catalyst metal thin film
  - Metal droplet acts as seed for nanowire

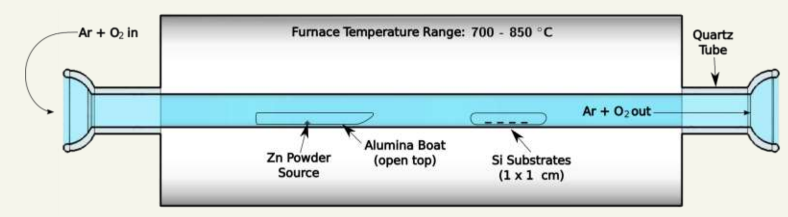


Schematic of VLS growth [5]

- Has been used successfully for ZnO aligned nanowire array synthesis [6,7]
  - Zn powder and O_2 gas source materials
  - Results are strongly dependent on experimental conditions and particular sample geometry [8]

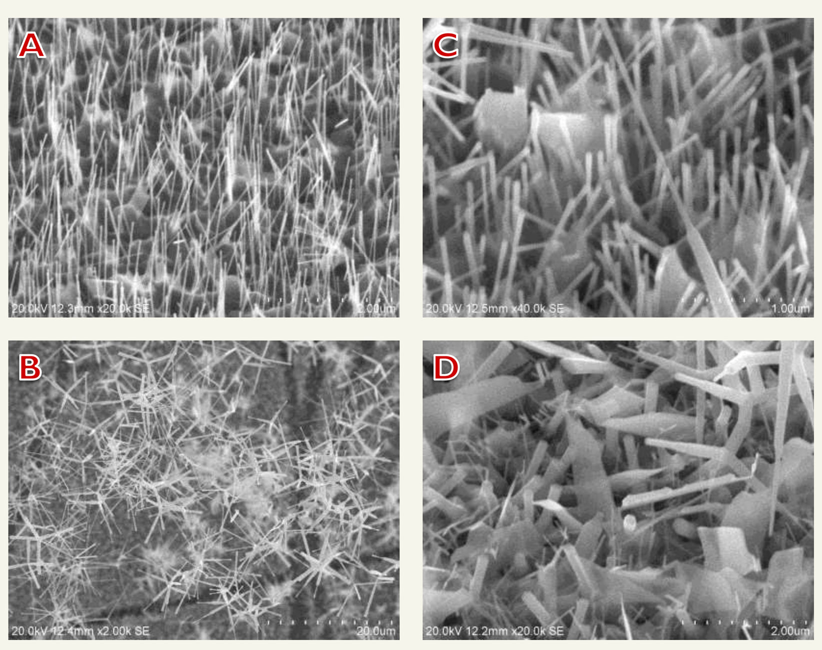
- Growth parameters investigated in this study:
  - Total gas flow rate (O_2 + Ar carrier gas)
  - Relative gas flow rates (Ar:O_2 ratio)
  - Timing of gas release
  - Mass of Zn source powder
  - Geometry of interior components
    - Affects substrate temperature and local P_{O_2} and $P_{Zn(v)}$

Experimental Setup



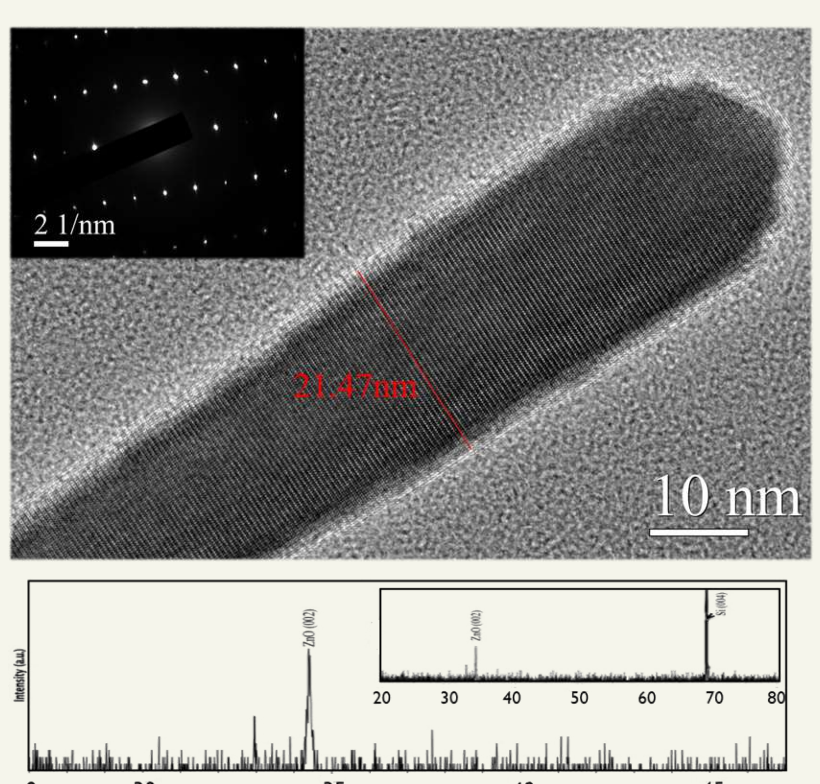
- Horizontal tube furnace (P: 1 atm)
- Source Zn and substrates in alumina boats
- Au thin film catalyst layer (2 nm)
- Si (001) wafer with native SiO_2 oxide layer
- Inert Ar carrier gas
- $T = 700 - 850°C$

Common Nanowire Array Growth Morphologies



A. Uniform diameters; narrow wires grow from textured ZnO film
B. Tetrapod "overgrowth" extended above nanowire growth
C. Thicker diameters; inferior alignment; non-uniform shape and size
D. Mix of "nanobelts," "nanorods," tetrapods, and "nanoribbons"

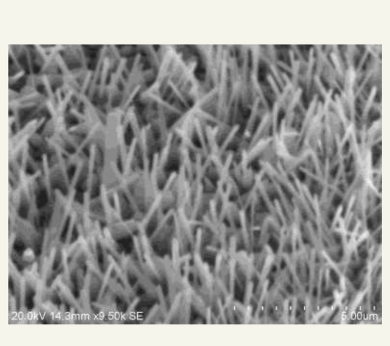
Nanowire Array Crystallinity

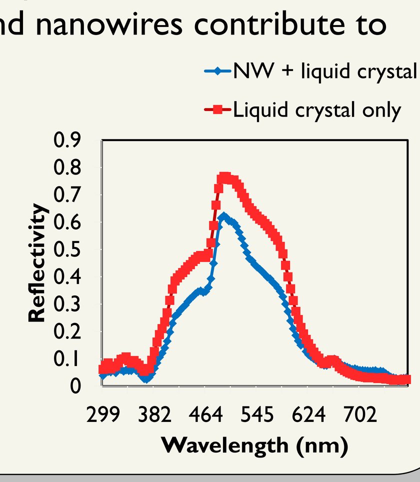


- HRTEM and XRD:
  - Nanowires are high quality and single-crystalline
  - Grow along [0001] direction
  - Fairly uniform diameter
  - No evidence for VLS growth (metal at tip)

Reflectivity: Nanowires with Liquid Crystal

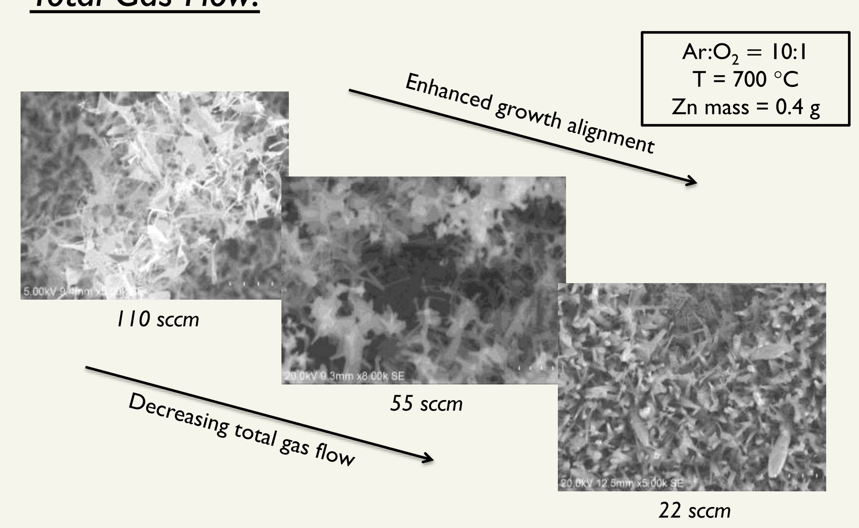
- Preliminary reflectivity measurements
  - Using poorly-aligned but uniform 200 nm diameter array
  - Measure pure liquid crystal and hybrid system
  - Witnessed decreased reflection
  - ↓ reflection = ↑ absorption
  - Both liquid crystal and nanowires contribute to photoabsorption





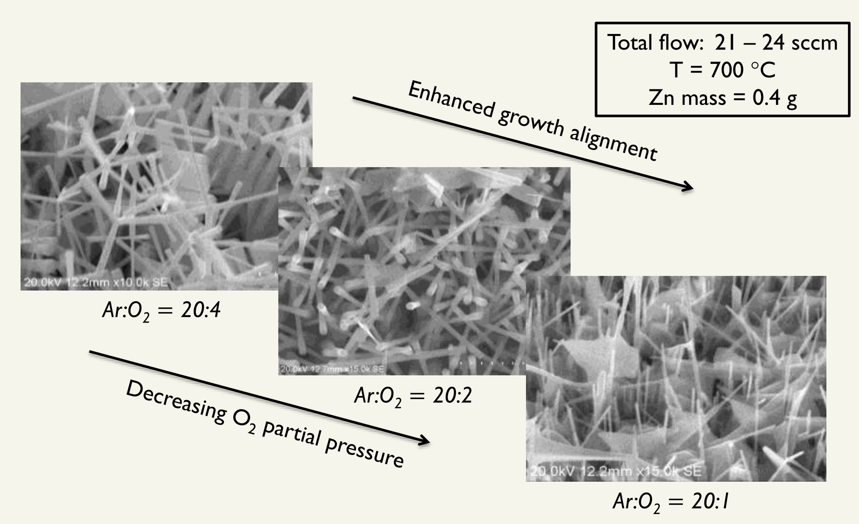
Effect of Growth Conditions

Total Gas Flow:



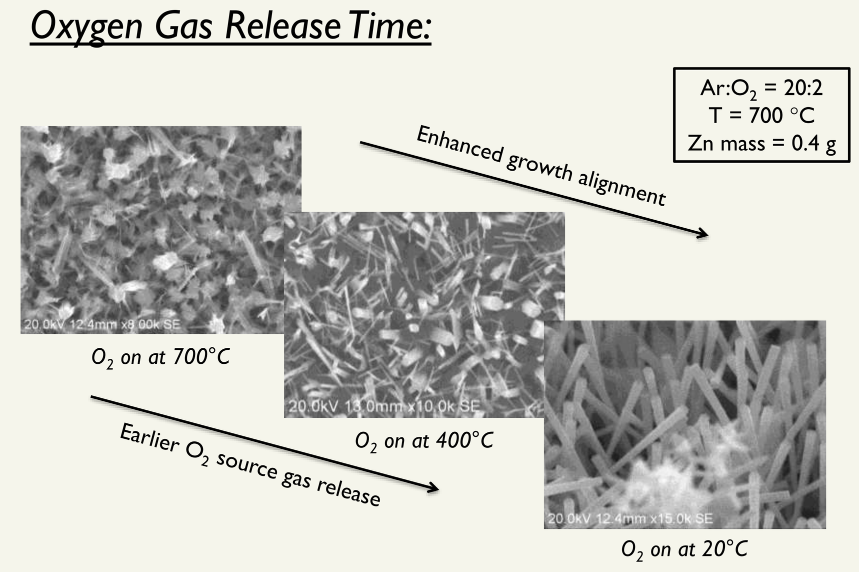
- Lower flow rates decreases branching and allows for more controlled growth

Relative Gas Flow Ratio:



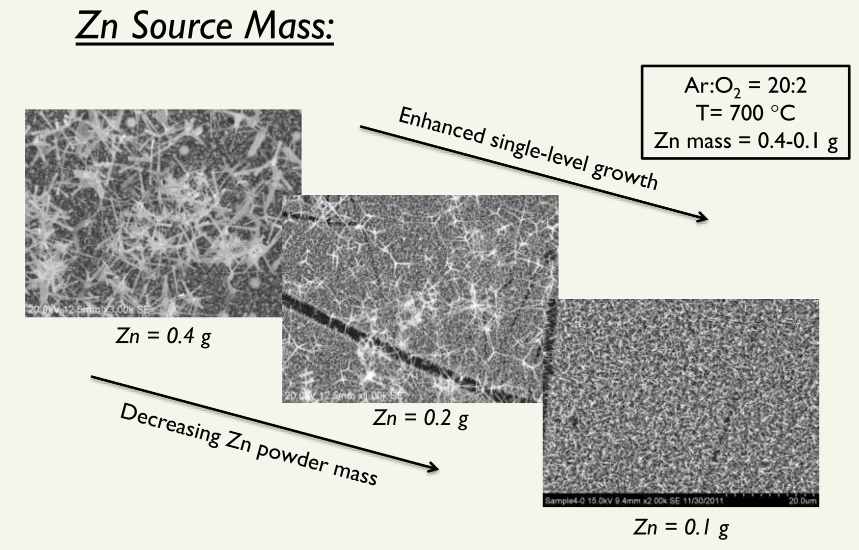
- Lower oxygen partial pressure suppresses tetrapod overgrowth and encourages vertical wire alignment

Oxygen Gas Release Time:



- Earlier gas release improves uniformity and nanowire shape/alignment → steady state growth
  - Oxidation of source before melting can prevent Zn vapor formation if not enough Zn source used

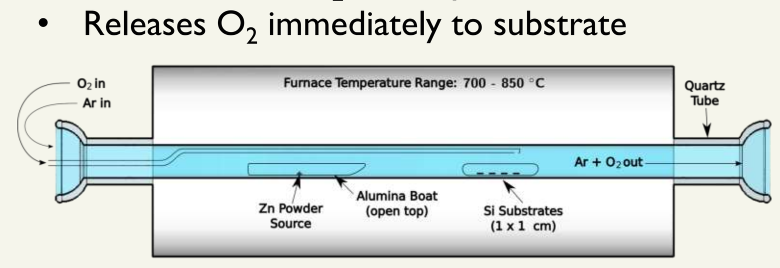
Zn Source Mass:



- Reduced source mass discourages top-level overgrowth and improves uniformity, to a point
  - Too little Zn source can cause early oxidation and prevent evaporation into Zn vapor

Alternate Synthesis Design

- When using low source mass (0.2 g and below) and earlier O_2 gas release, Zn source has tendency to oxidize with a skin, preventing evaporation
- Introducing O_2 directly at substrate allows for finer control of growth conditions:
  - Geometry and local P_{O_2} can be finely controlled
  - Oxidation of source is prevented
  - Greater flexibility in localized conditions
- Design after J. Park *et al.* [9]:
  - "Showerhead" O_2 delivery
  - Releases O_2 immediately to substrate



Preliminary Results:
- Showerhead prevents source oxidation
- Did not immediately observe VLS as in [9]
- Changing internal geometry significantly affected growth results (need further optimization)

Conclusions

- Setup reproducibly grows ZnO nanowire arrays
  - Vertical alignment needs improvement
  - VLS mechanism not active
- Growth results are heavily dependent on a wide range of experimental parameters
  - Localized conditions greatly affect results, e.g., Zn vapor pressure, O_2 partial pressure
- *Most promising conditions:*
  - Lowest possible flow rates (less turbulence)
  - Lowest P_{O_2} (lowers oxidation rate)
  - Earlier O_2 release (steady state conditions)
  - Less Zn source (reduces Zn vapor saturation)
- Approaching optimized conditions for VLS growth
  - "Showerhead" O_2 delivery shows great promise
- Optical absorption is higher when nanowires are combined with liquid crystal

Future Work

- Further investigation of new furnace geometry
- Characterize effect of other growth parameters:
  - Total chamber pressure
  - Substrate/source temperature
  - Distance between source and substrate
  - Growth time and furnace heating rate
- Fabricate proof-of-concept devices
- Measure photoconductivity of ZnO nanowires with liquid crystal
- Characterize liquid crystal orientation effect of nanowires relative to ZnO nanoparticles

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