Pyrite Thin Films: Nanocrystal Films and Molecular Processing

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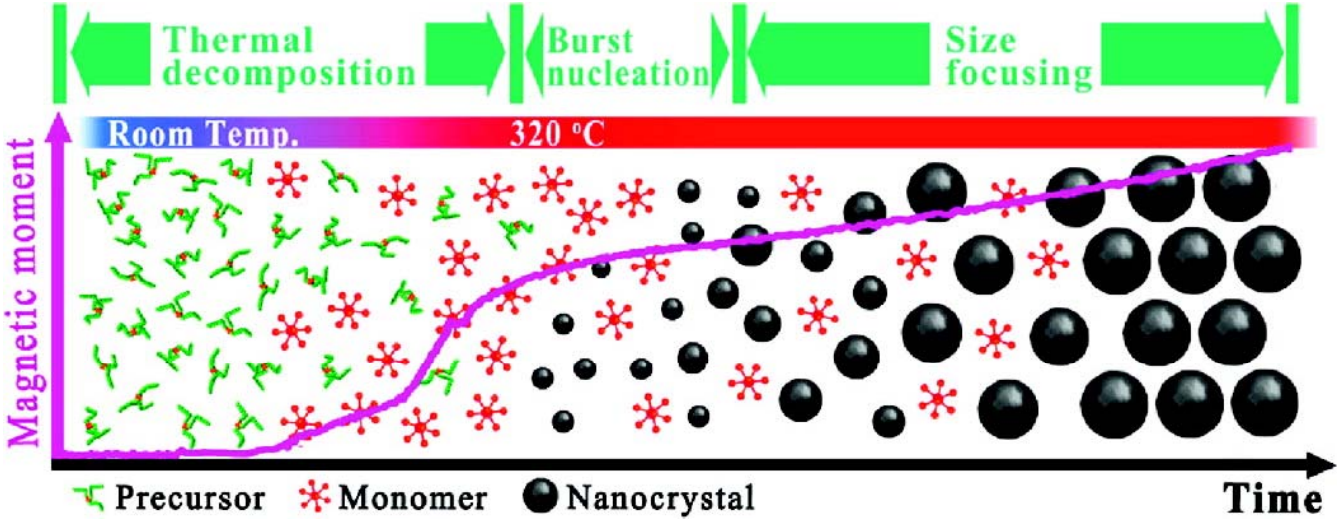
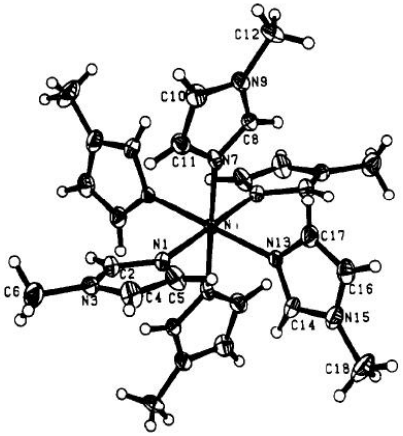
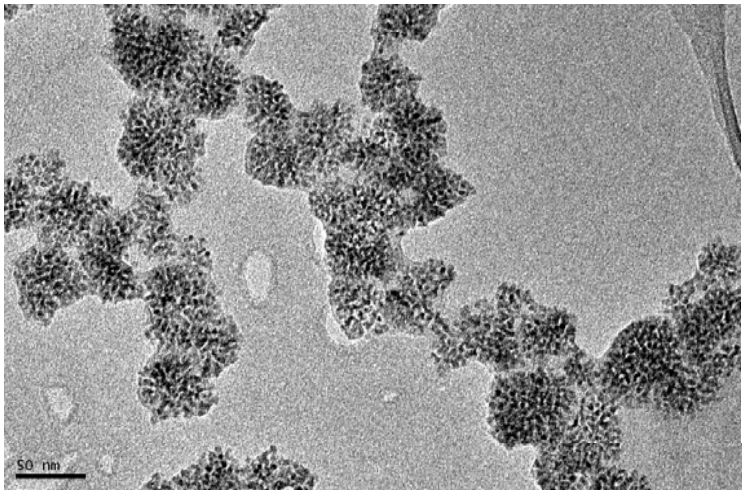
Nanocrystal Solvothermal Synthesis







Published in: Soon Gu Kwon; Yuanzhe Piao; Jongnam Park; Subramanian Angappane; Younghun Jo; Nong-Moon Hwang; Je-Geun Park; Taeghwan Hyeon; *J. Am. Chem. Soc.* **2007,** 129, 12571-12584.

Nanocrystal Solvothermal Synthesis

- Hot Injection

  Injection of organometallic precursor into a hot surfactant solution

- Heating-Up

  Solution precursors separated by temperature in a one-pot synthesis

What are the Synthetic Difficulties?

- Crystal Phase Purity

  Phase is highly sensitive to solvent properties and precursor ratios

- Size Dispersion

  Reaction temperature and duration can determine the size distribution of nanocrystals

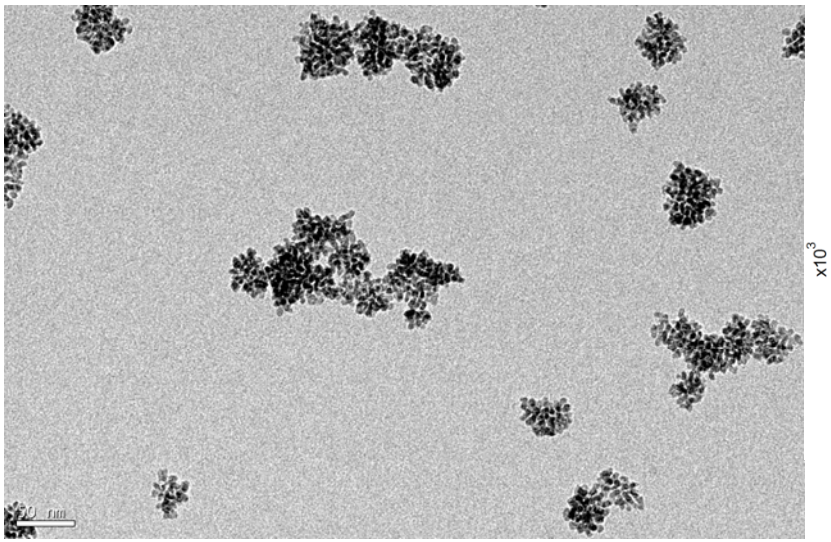
- Colloidal Suspension

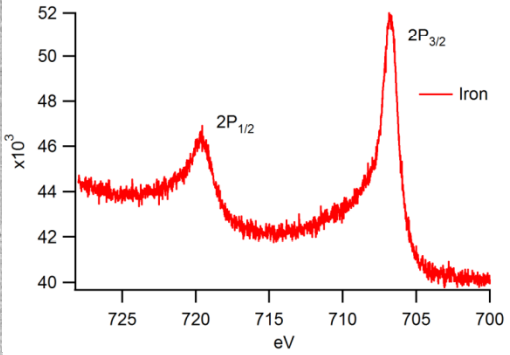
  Preventing aggregation and keeping nanocrystals in solution are key steps to obtaining “inks”

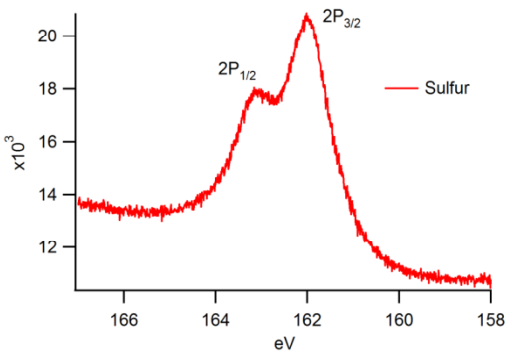
Pyrite Nanocrystal One-Pot Synthesis

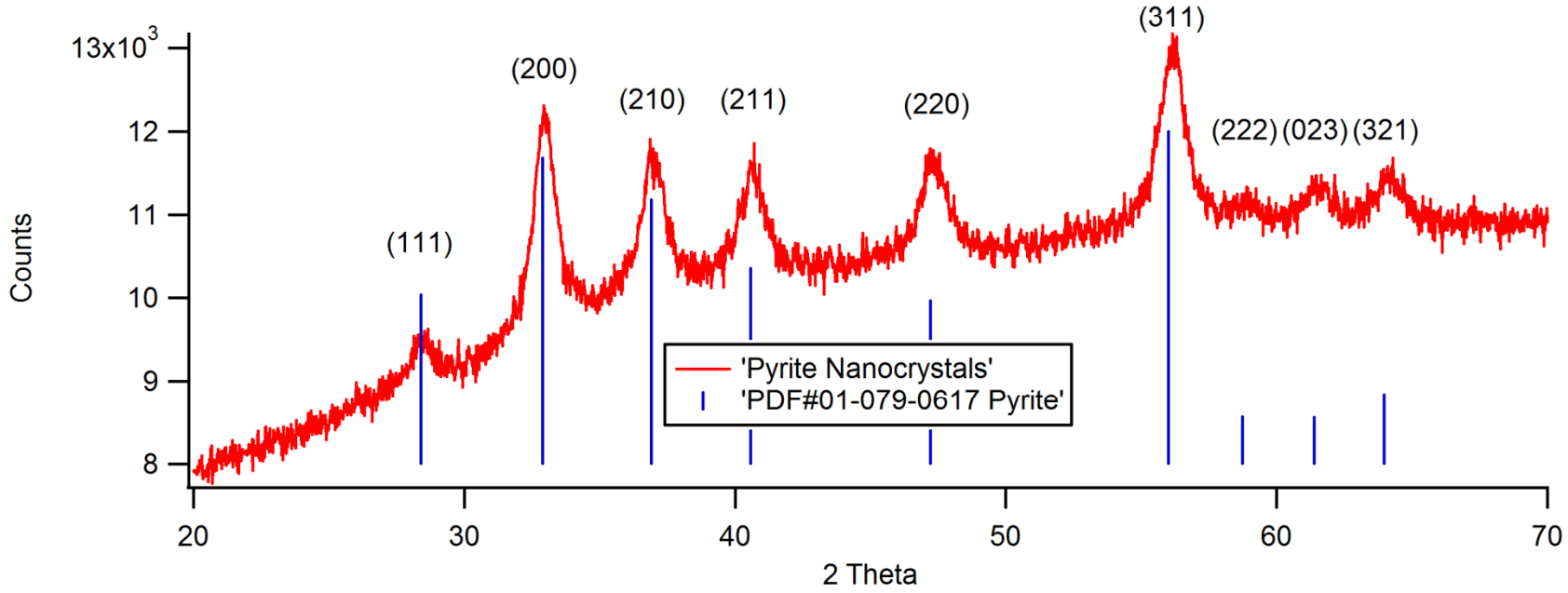
- 266mg of $Fe(N\text{-}MeIm)_6$ S_8 ,7.5g Octadecylamine, 400mg Sulfur
- Degass at 70 C (any higher will give poor results)
- React for 3 hours at 215 C and add 20mL of $CHCl_3$ at 80 C to prevent solidification of ODA
- Crashed out with ethanol and redispersed in chloroform.

Pyrite Nanocrystals

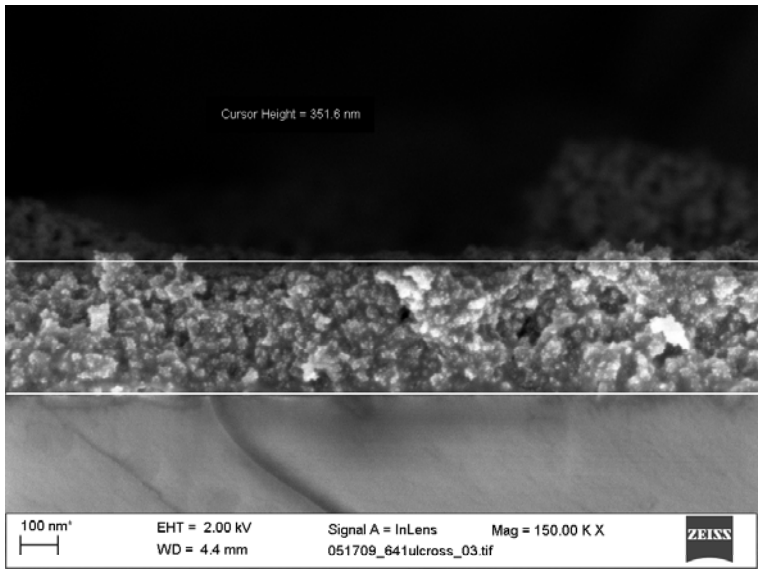








Pyrite Nanocrystal Films



Annealing Process:

Substrates are sealed in ampules with elemental sulfur in inert atmosphere

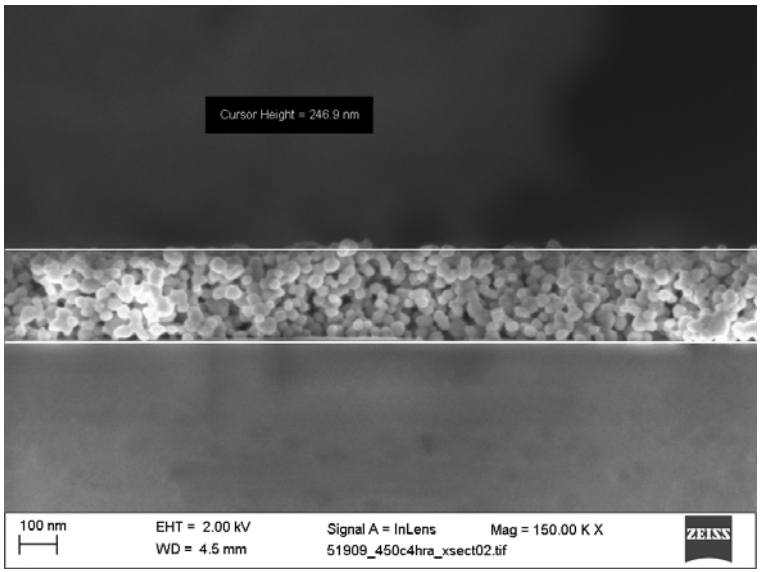
Ampules are then heated at the desired temperature and time to sinter nanocrystals into a film.

Dip Coating Process:

Substrate dipped into Nanocrystal “ink” solution

“Ink” coated substrate dipped into ligand exchange solution

Process repeated to build up thicker films



Pyrite Nanocrystal Issues

- Clustered nanocrystals do not deposit into films as easily as individual colloidal nanocrystals.
- Octadecylamine is currently not the ideal ligand for solution processing. (Requires $CHCl_3$)
- Nanocrystal solubility is highly sensitive to air, and can degrade over time.

Molecular Processing

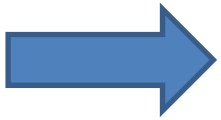
- High throughput, low-cost technique
- Thin films of pyrite directly produced on the desired substrate from iron and sulfur precursors.
- Direct processing onto substrates streamlines production.

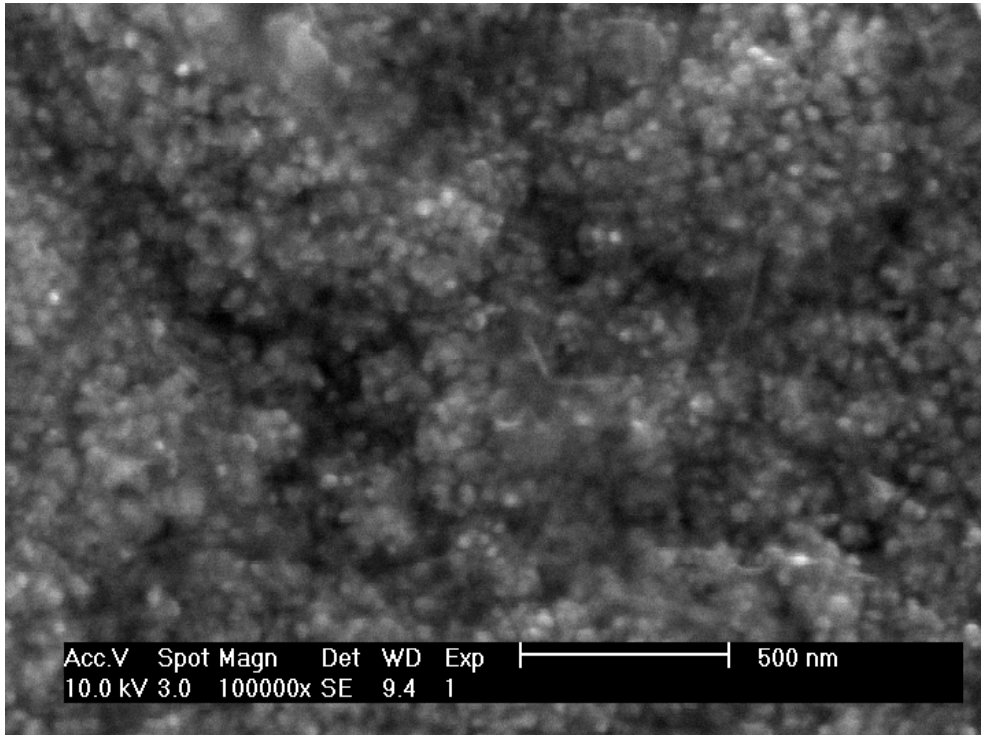
Pyrite Molecular Films

Contact

Glass

Deposit Precursors Directly





Bake Precursors in Sulfur Atmos.

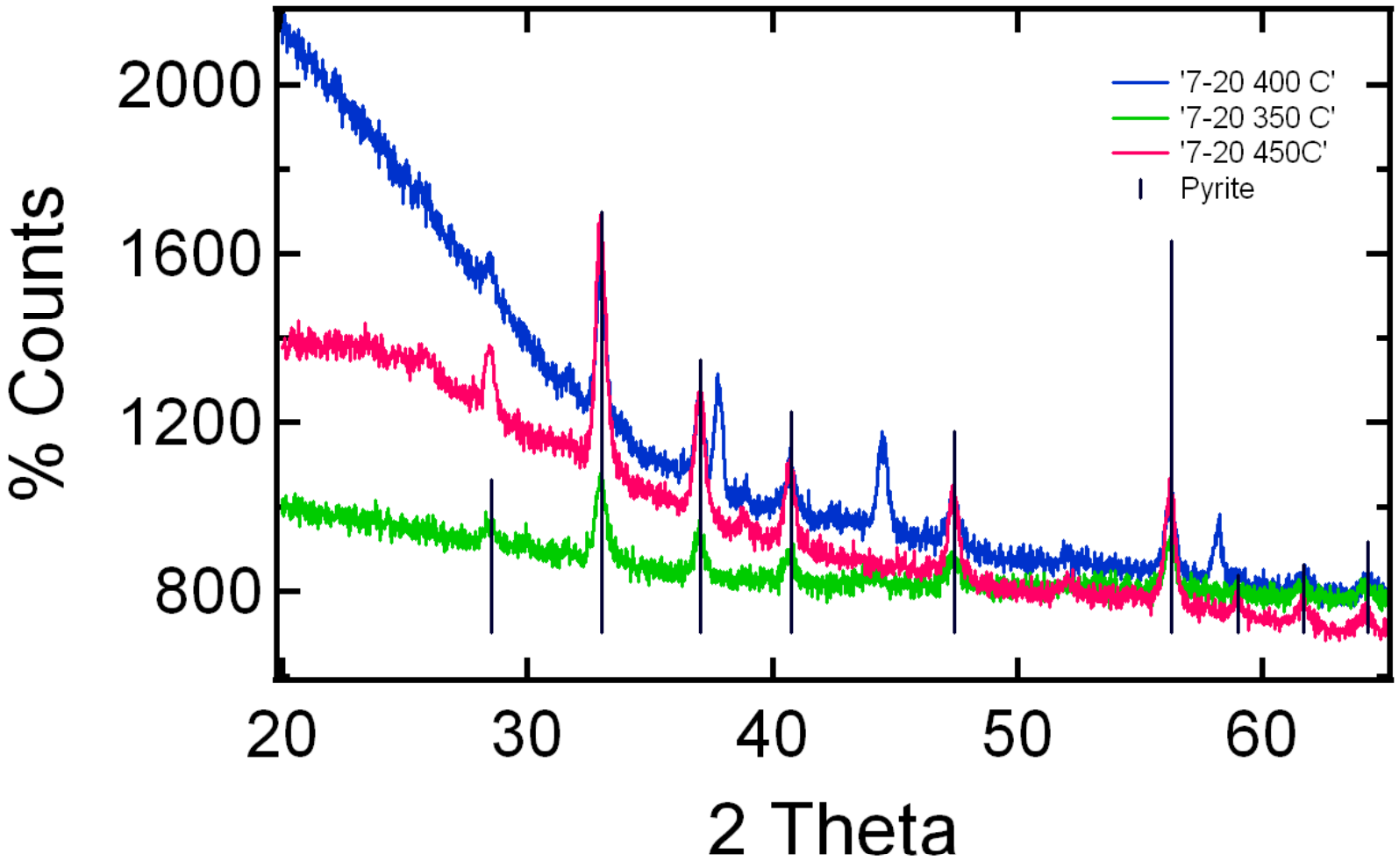
Pyrite Molecular Films

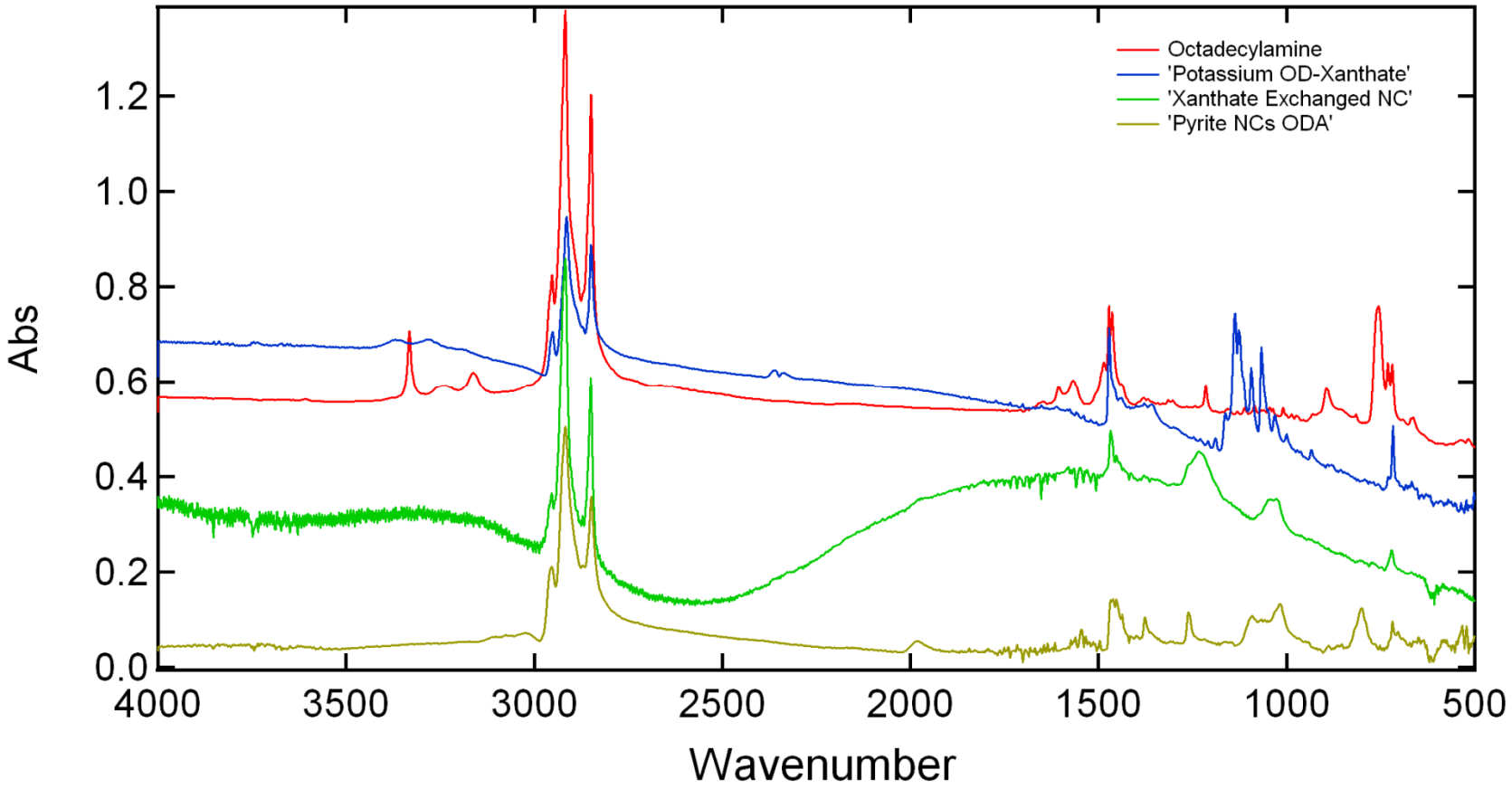
- Currently in the early stages.
- Polycrystalline small grain pyrite films have been made.
- Final film morphology is directly controlled by precursor film morphology.
- Film morphology should be easily controlled by solution concentrations and viscosities.

Pyrite Molecular Film Issues

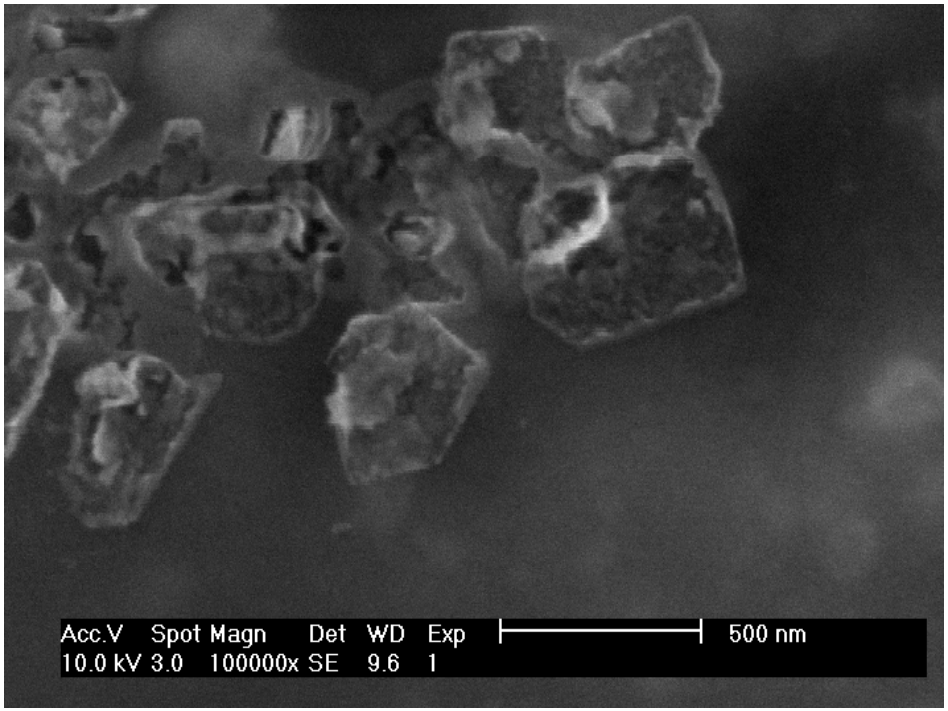
- How will precursor selection affect device performance?
  - Impurities
- How will these processes scale?
  - Doctor Blading/Roll-to-Roll vs Spin Coating

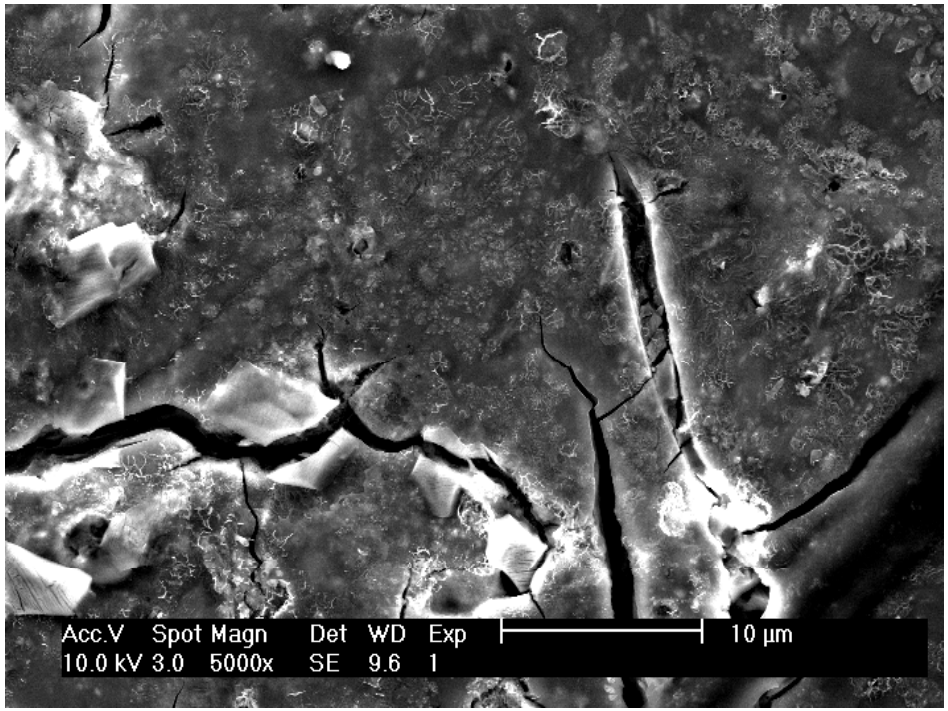
- Backup Slides


% Counts
2000
1600
1200
800
20
30
40
50
60
2 Theta
'7-20 400 C'
'7-20 350 C'
'7-20 450C'
Pyrite


Octadecylamine
'Potassium OD-Xanthate'
'Xanthate Exchanged NC'
'Pyrite NCs ODA'
Abs
0.0
0.2
0.4
0.6
0.8
1.0
1.2
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber

- Before Annealing





- After Annealing