Iron Sulfur Molecular Inks for Pyrite Thin-Films

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Pyrite Collaboration Meeting

12-7-2010

Outline

- Motivation
- Synthesis
- H_2S annealing
- S_2 annealing
- Future Work

Motivation for Molecular Inks

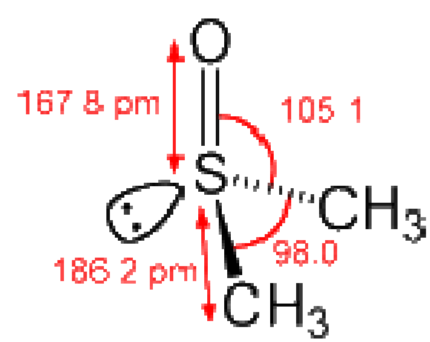
- **<u>Goal:</u>** Find a convenient method for film deposition that has the correct composition, phase purity, and grain structure

- Benefits of Using Molecular Ink approach:
  - Solution based approaches are easier to scale up
  - Well controlled stoichiometry and minimal to no contamination (elemental precursors)
  - Simple film deposition (spin casting, doctor blading, drop casting)

Using dimethyl sulfoxide (DMSO) and ethanolamine as a solvent mixture to dissolve elemental precursors

- **Motivation:** Paper by Mitzi stating that a mixture of DMSO and ethanolamine was an effective wetting agent for thermally oxidized silicon substrates; <u>less toxic than hydrazine</u>

- **Previous molecular ink approaches:**
  - CZTS (copper zinc tin sulfur/selenide) films: Dissolved elemental precursors in hydrazine and obtained devices with over 9.6% efficiency (as opposed to previously obtained efficiencies of 3.2% and 6.7%)
  - CIGS (copper indium gallium sulfur/selenide): ‘’ ‘’ in hydrazine and obtained efficiencies of 10.1%



D. B. Mitzi, Adv. Mater, 2009, 21, 3141-3158.
Wikipedia.com

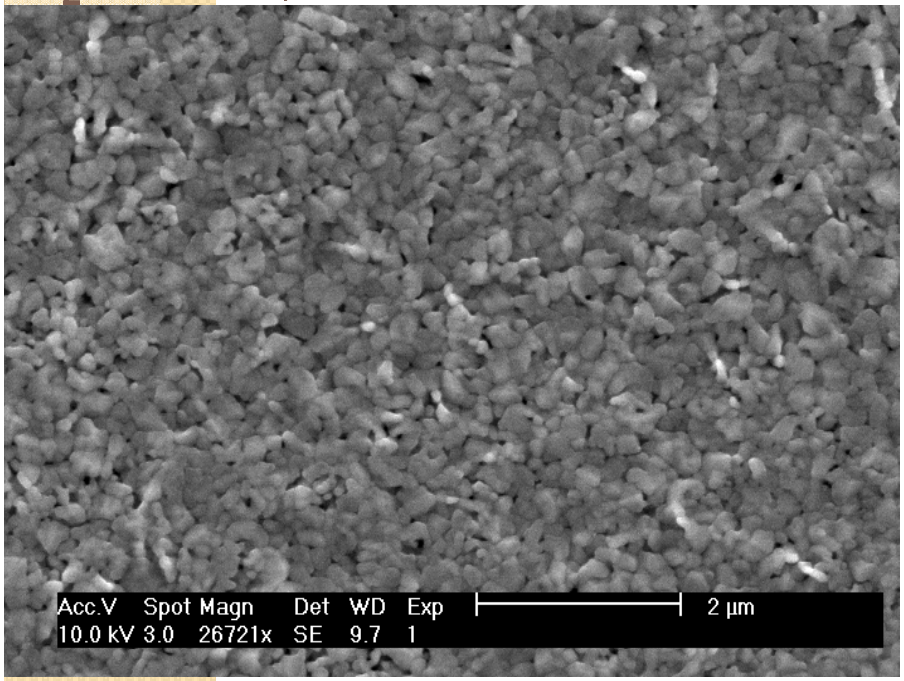
Synthesis Process Inside N_2 Glovebox

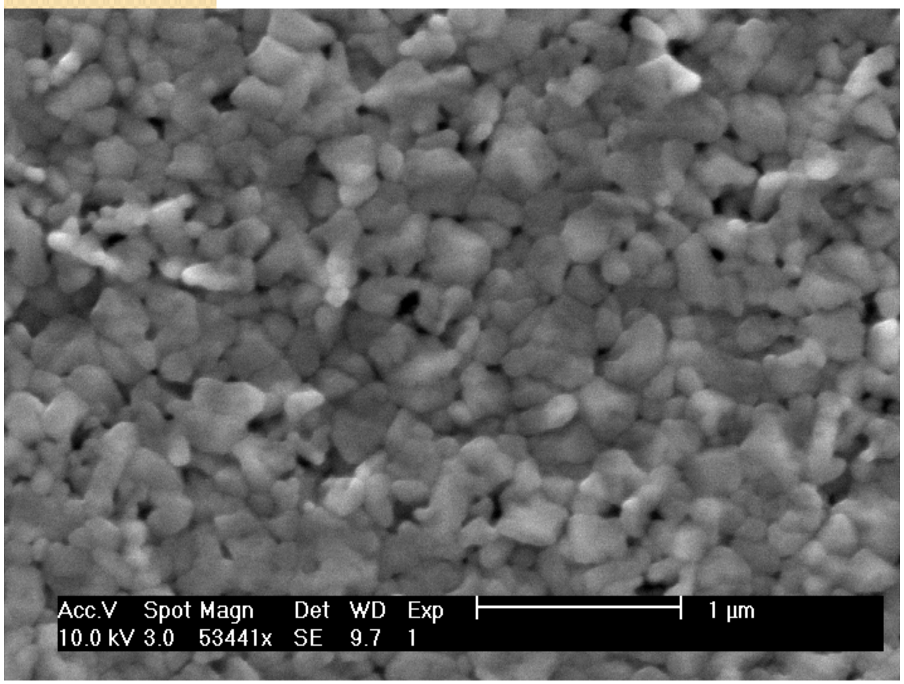
- Each layer is roughly 150 nm

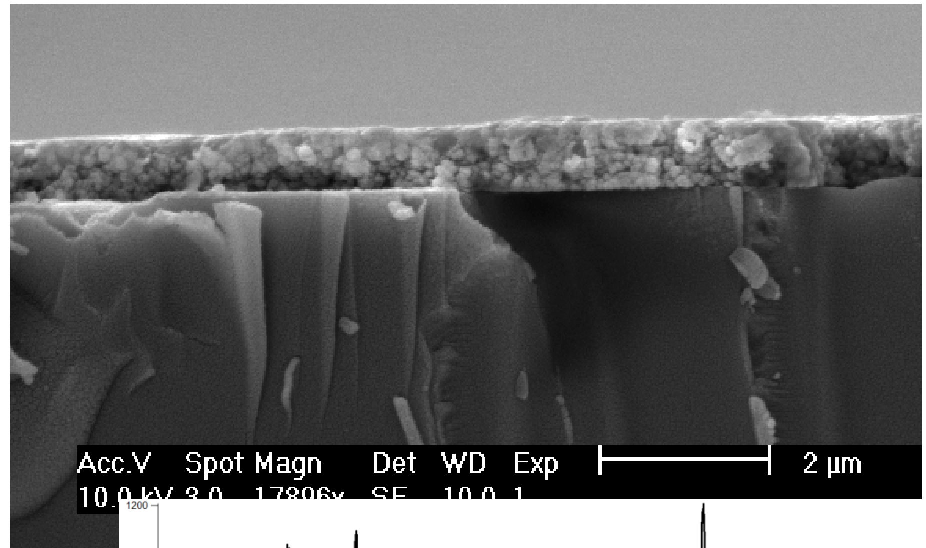
- 200℃ is ideal pre-baking temperature since the boiling points of DMSO and ethanolamine are 189℃ and 170℃ respectively; by FT-IR all organics seem to be removed

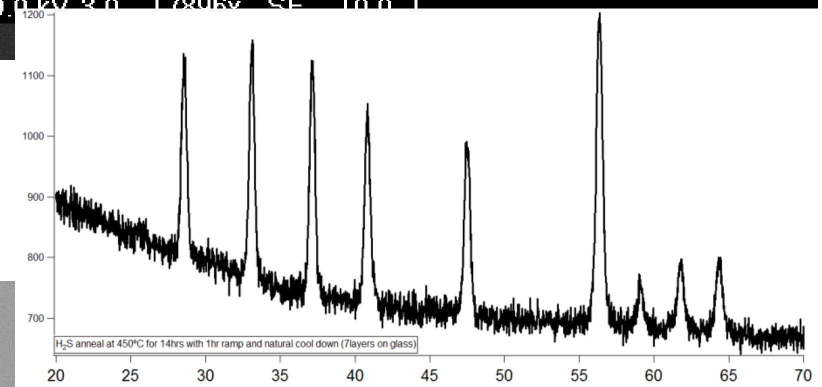
1. **Form mixture of DMSO and ethanolamine (6.5:1)**
2. **Dissolve S (1 M) in solution and stir for >6 hours (at room temp)**
3. **Add Fe (0.33 M) and stir for >24 hrs.**
4. **Spin coat at 1500 rpm for 60s**
5. **Pre-bake on hotplate at 200℃ for 5 min.**
6. **Anneal in S (25 mg) at 550° C for 6 hours**

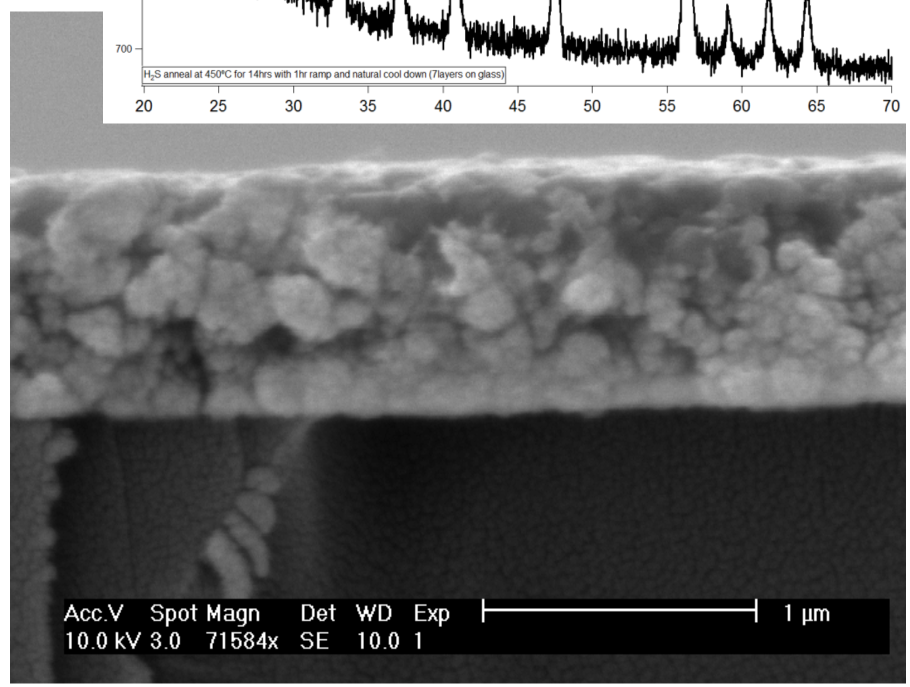
H_2S 450℃, 15hrs



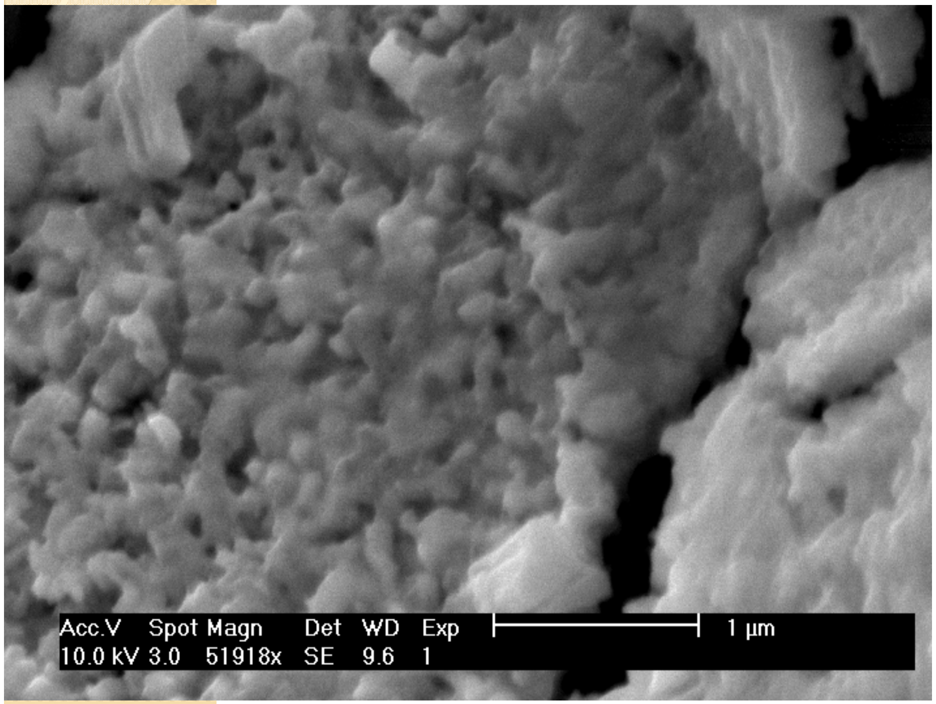


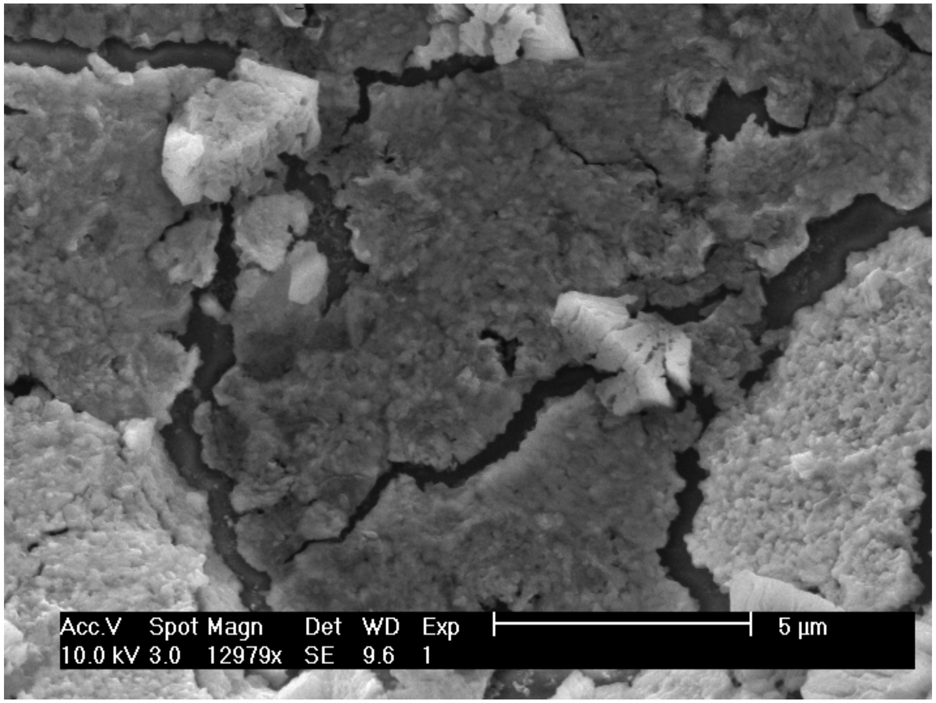


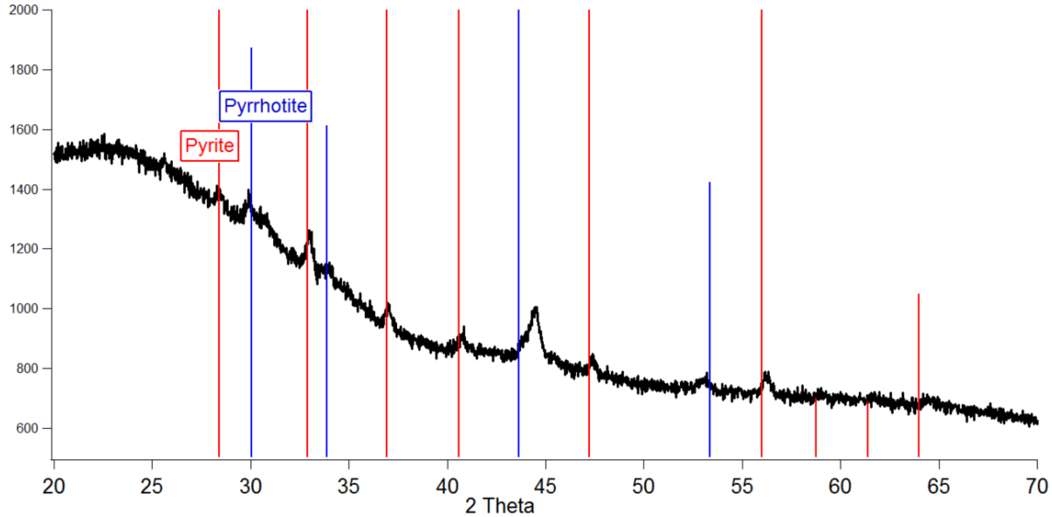


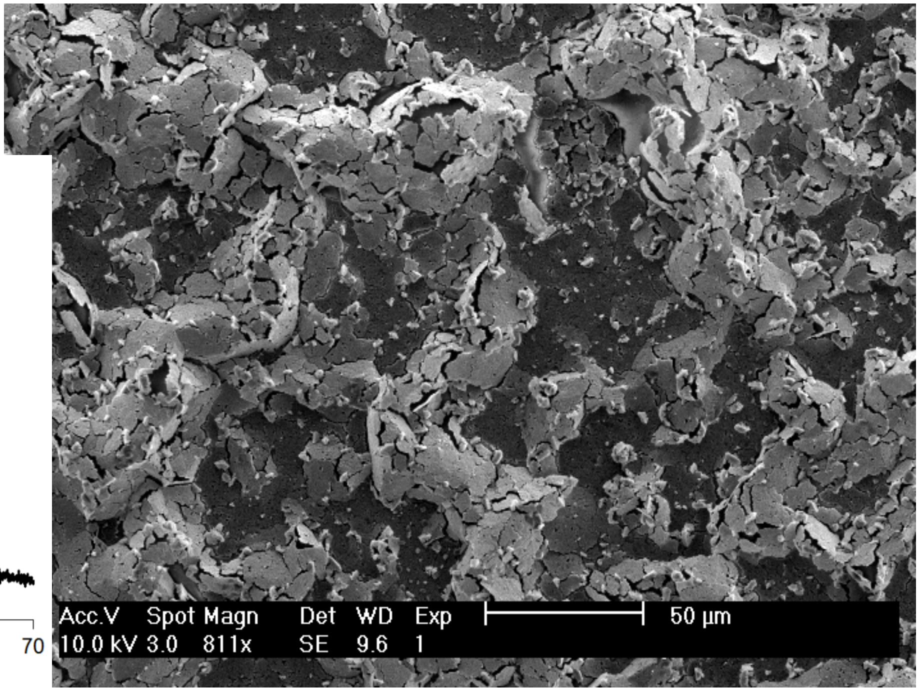


H_2S, 500 ℃, 15hrs

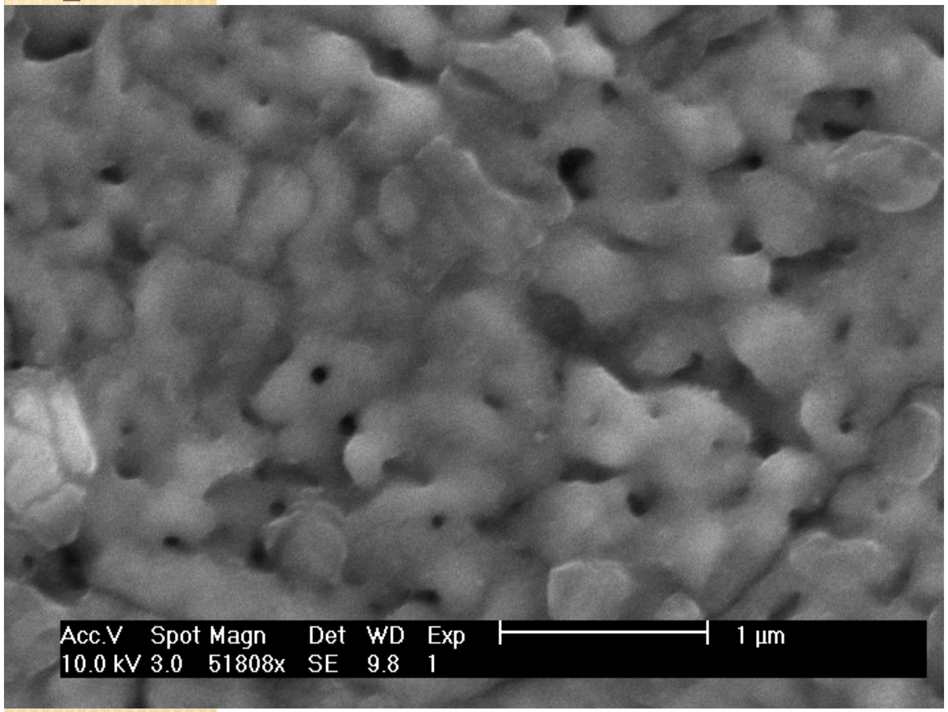


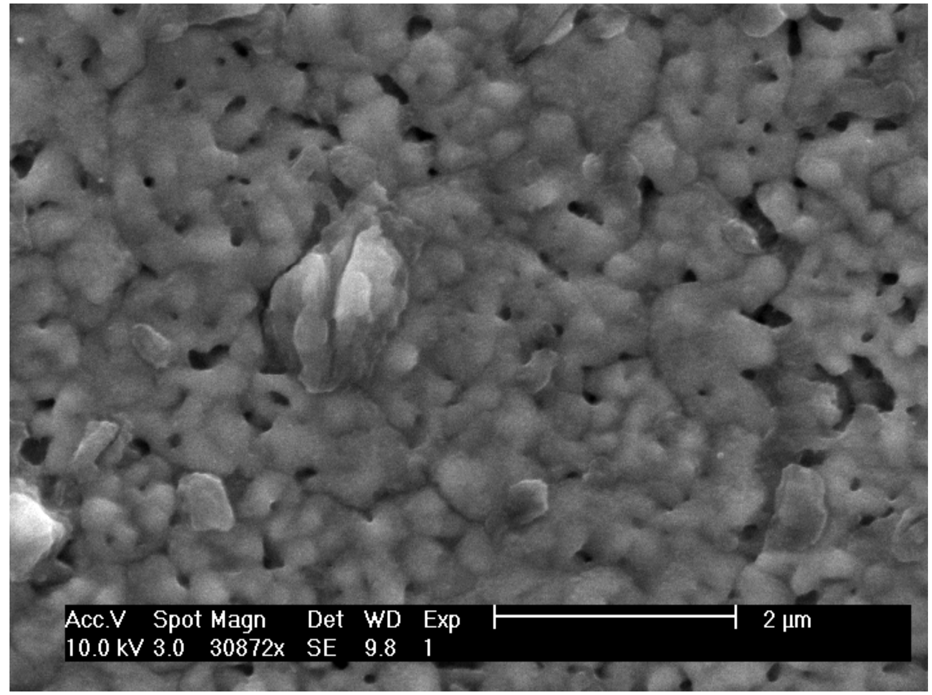


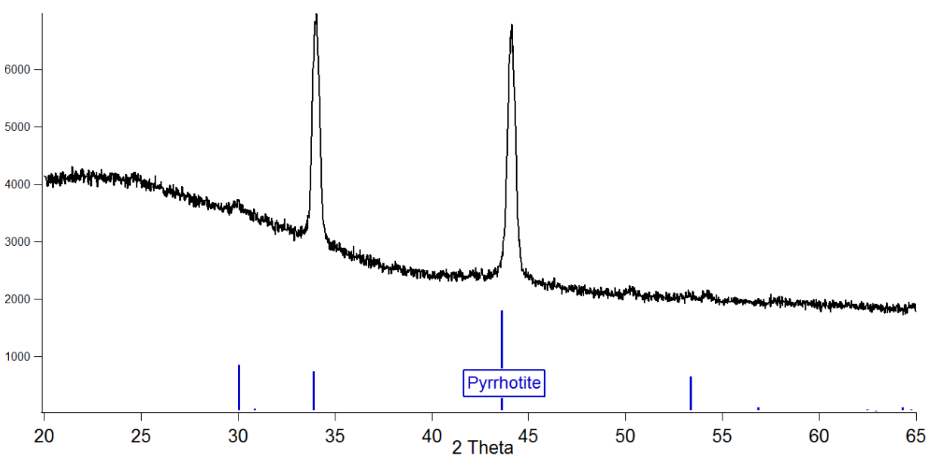


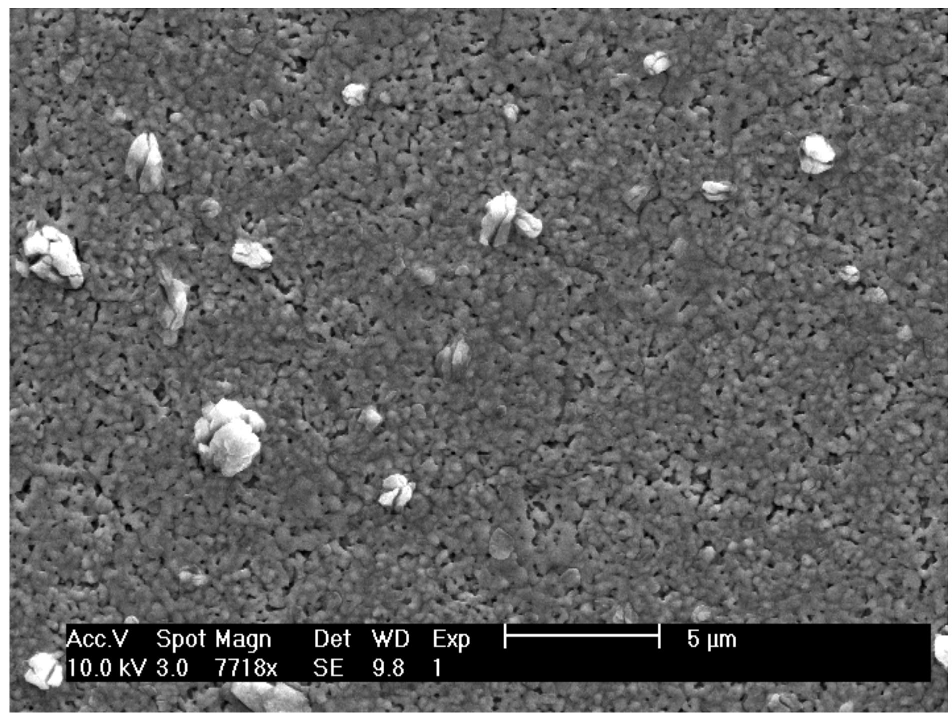


H_2S, 550℃, 15hrs

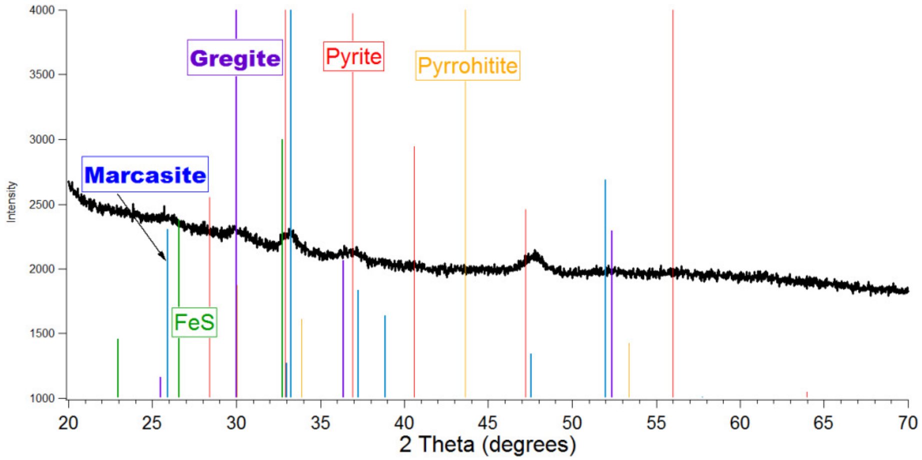


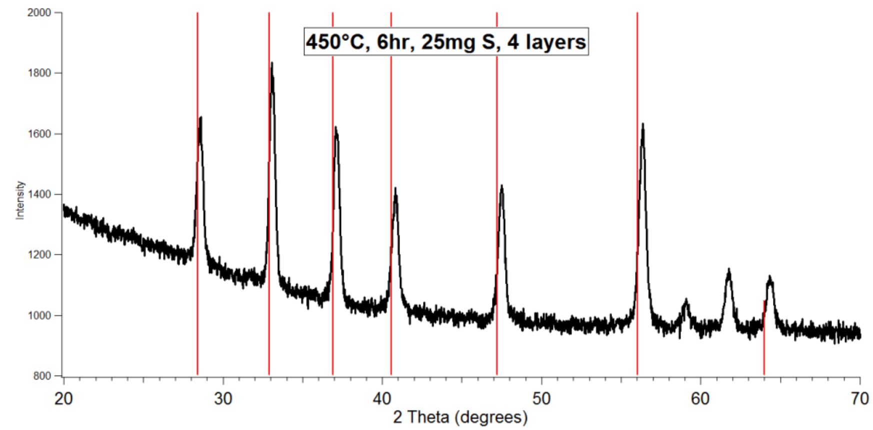


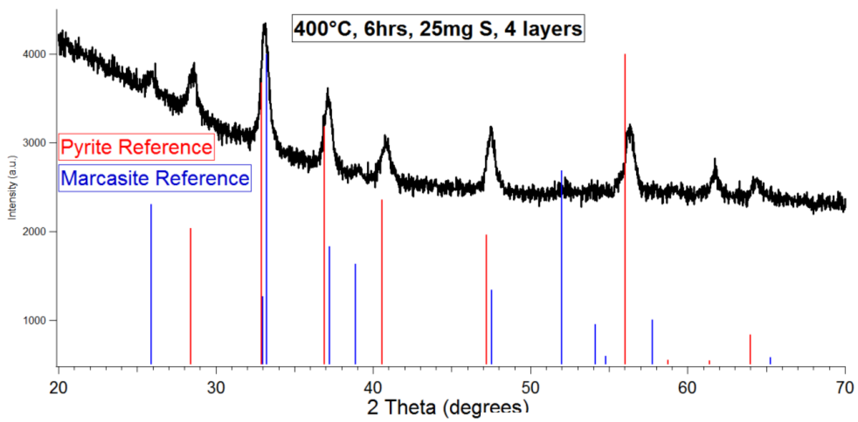


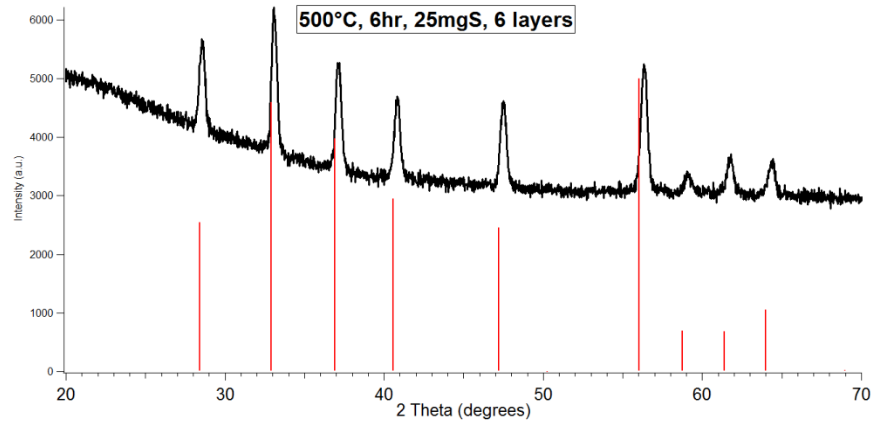


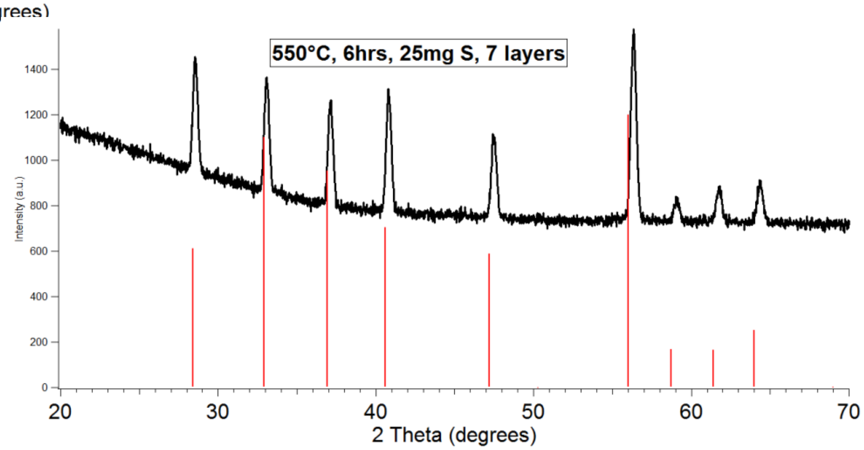
S_2 Annealing X-Ray Diffraction Patterns







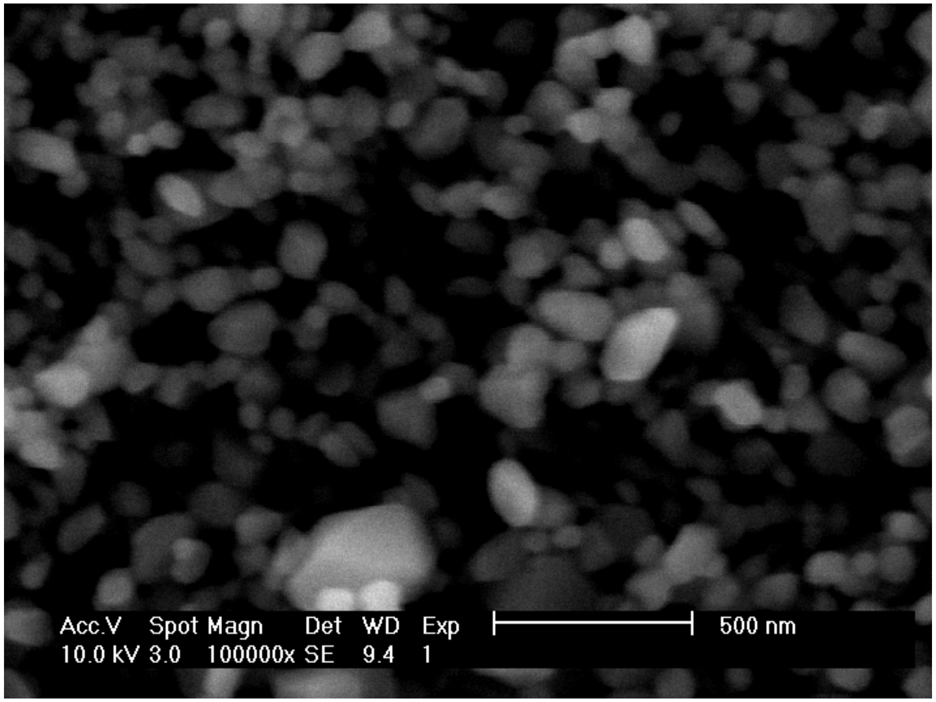


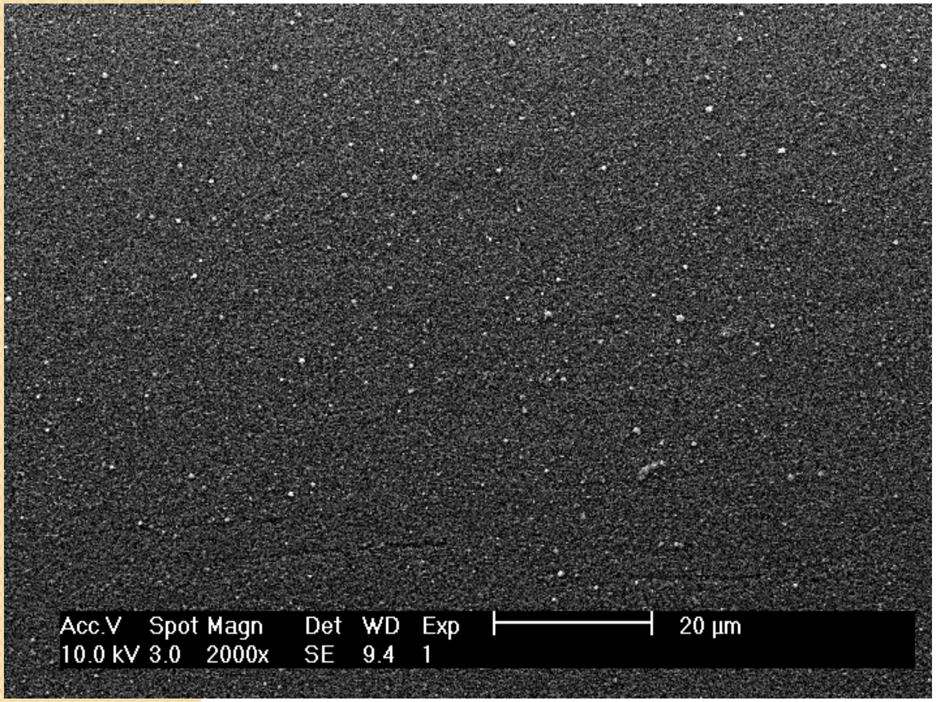


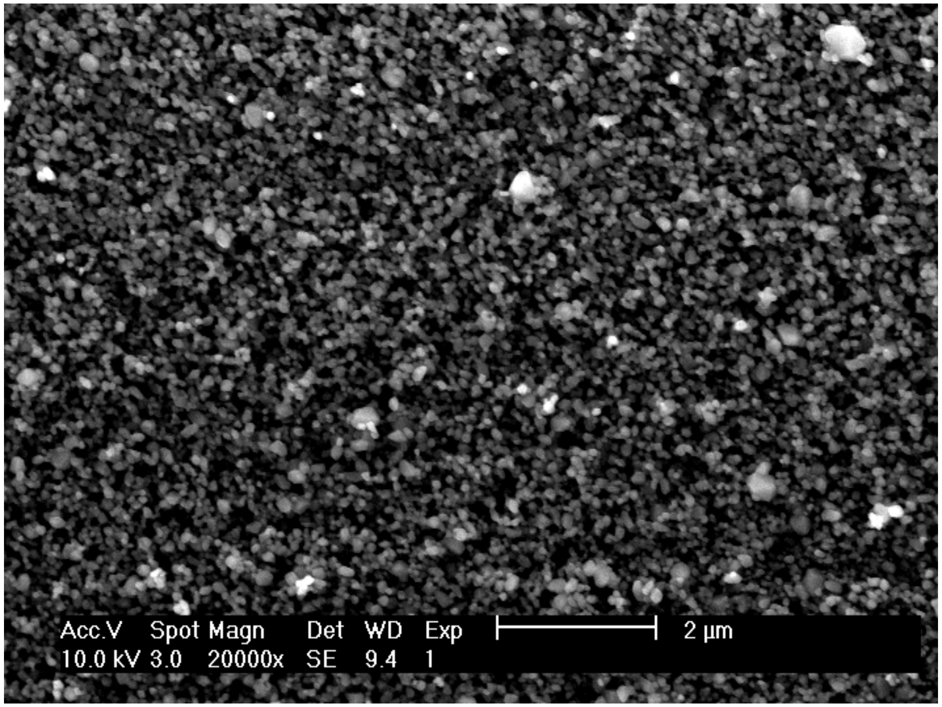
500℃, 6hrs, 25 mg S

• Yields pure pyrite, but morphology is not ideal

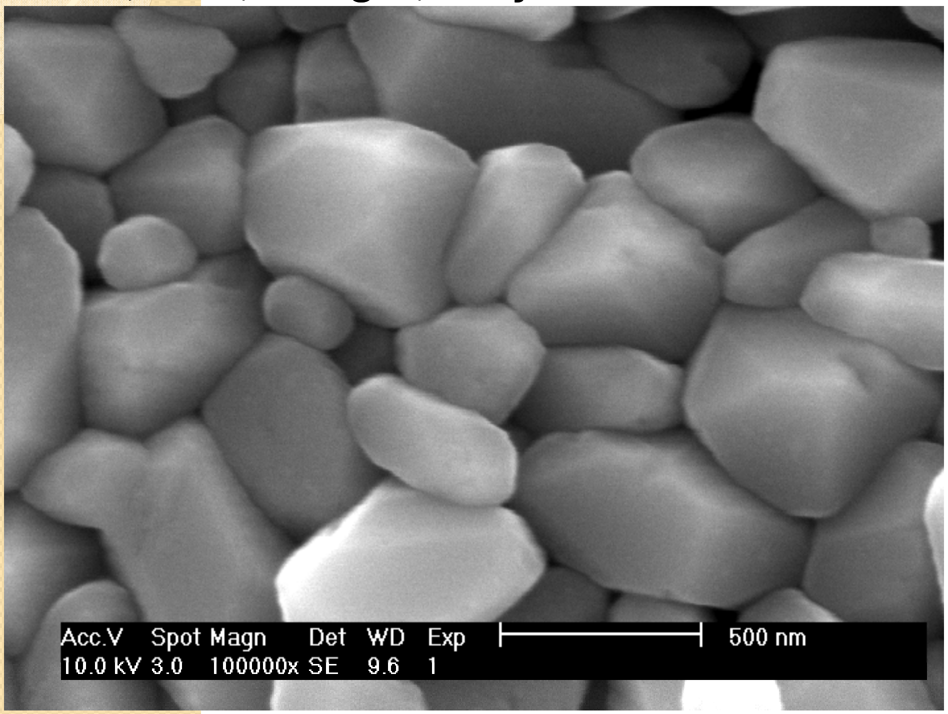
- Little grain growth
- Not well connected grains

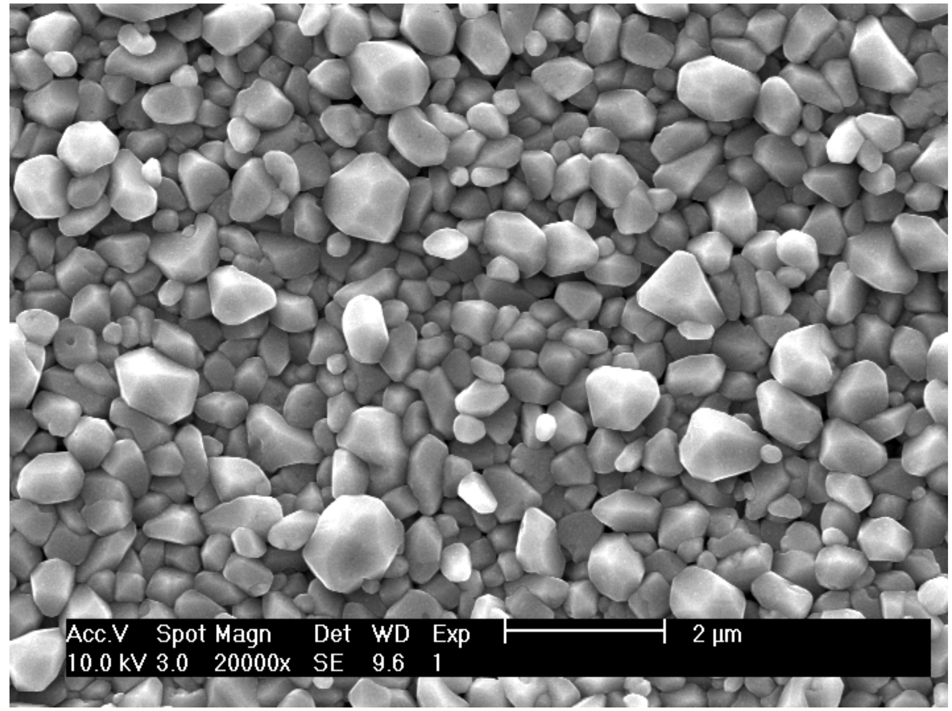


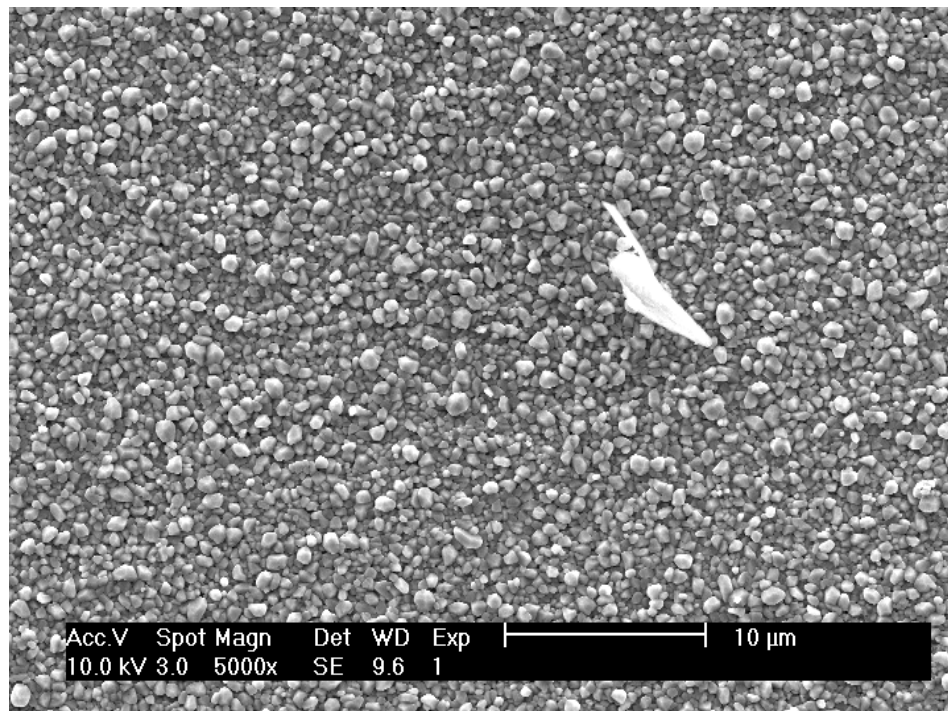




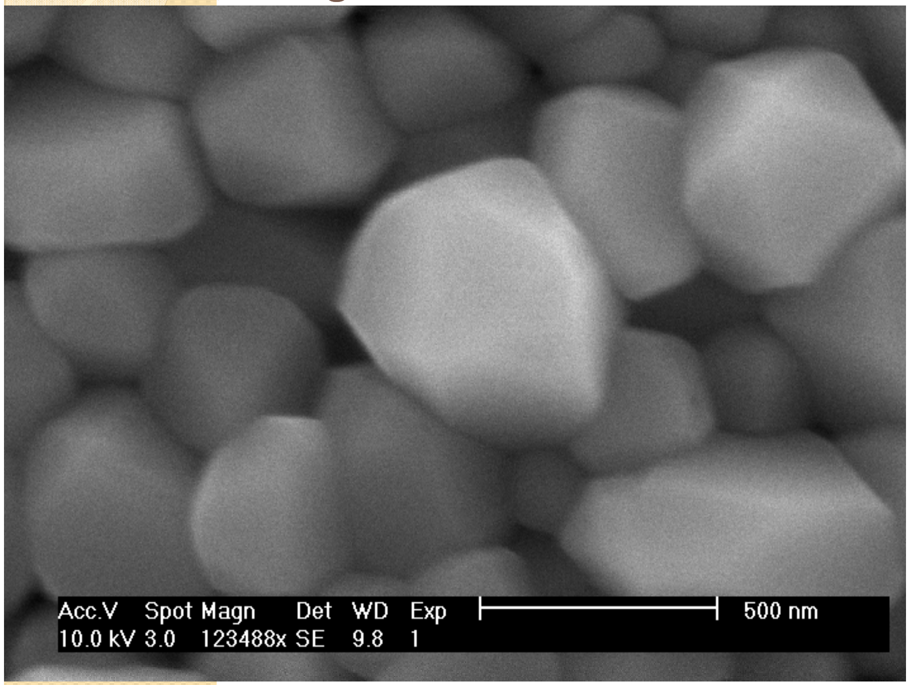
550 ℃, 6hrs, 25mg S, 7 layers

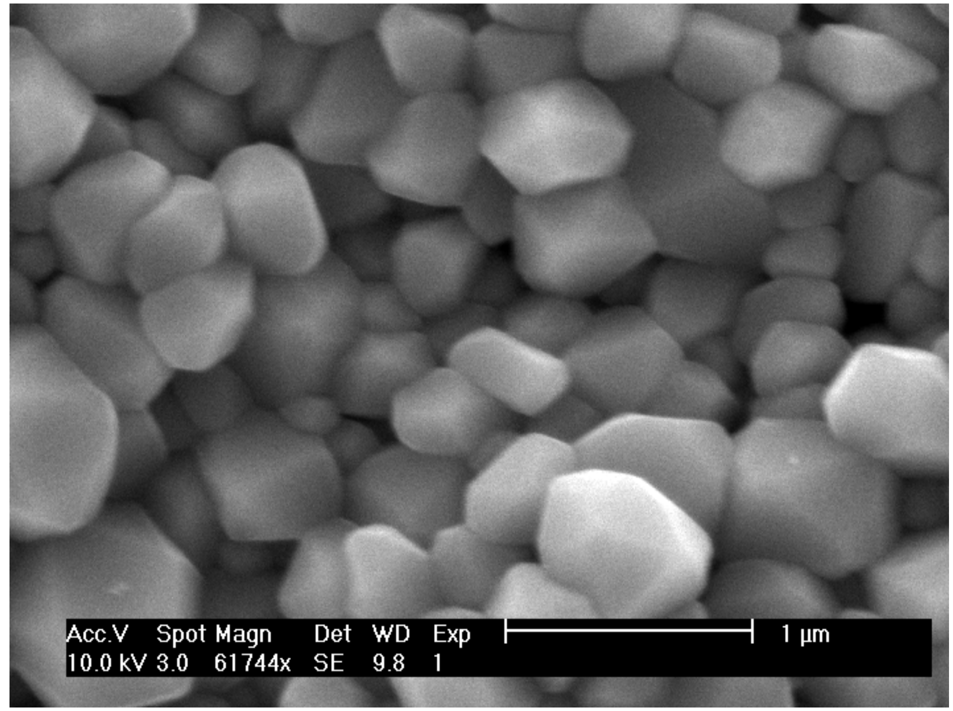






600℃, 6h, 25mg S


Acc.V Spot Magn Det WD Exp 500 nm
10.0 kV 3.0 123488x SE 9.8 1


Acc.V Spot Magn Det WD Exp 1 µm
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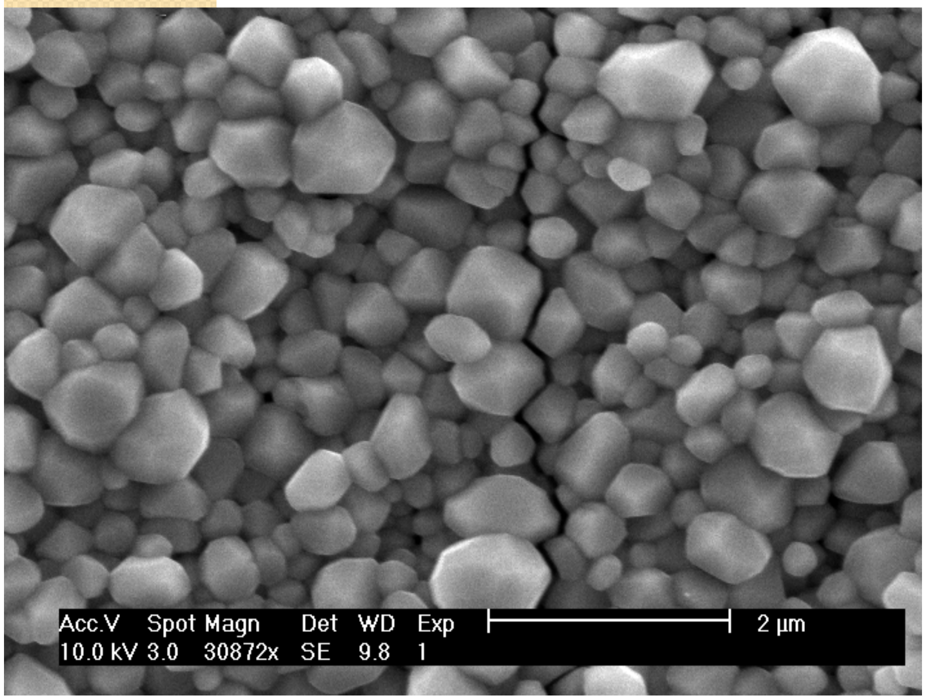
Acc.V Spot Magn Det WD Exp 2 µm
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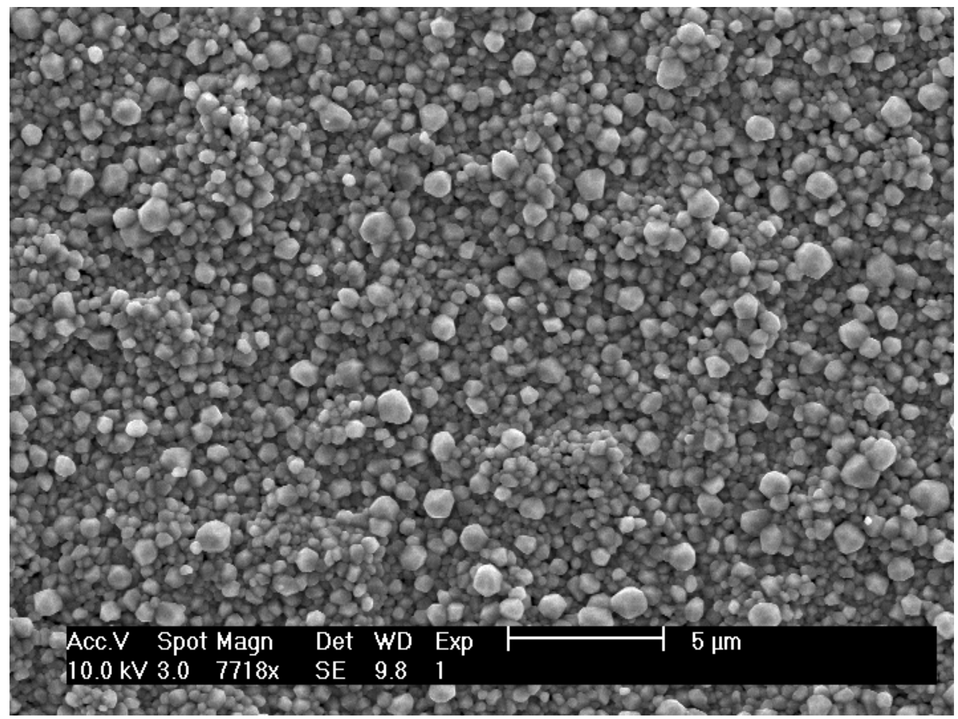
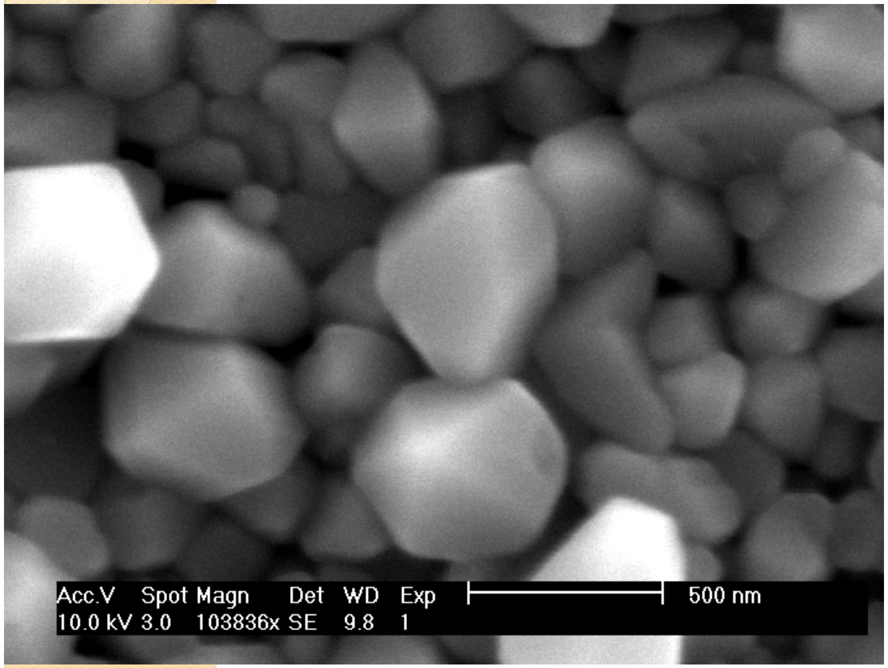
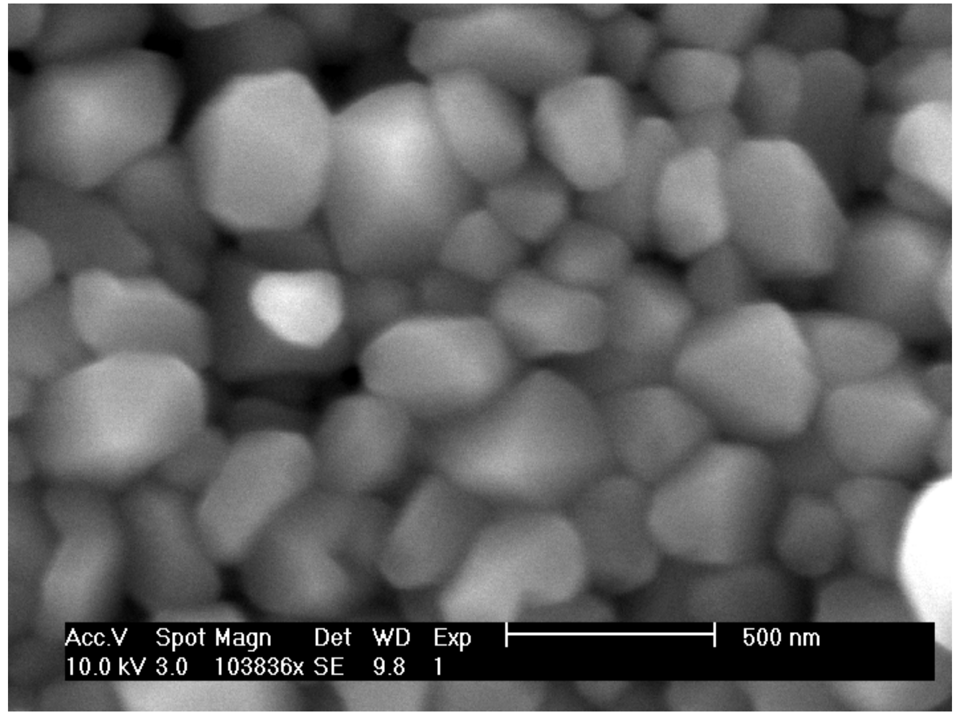
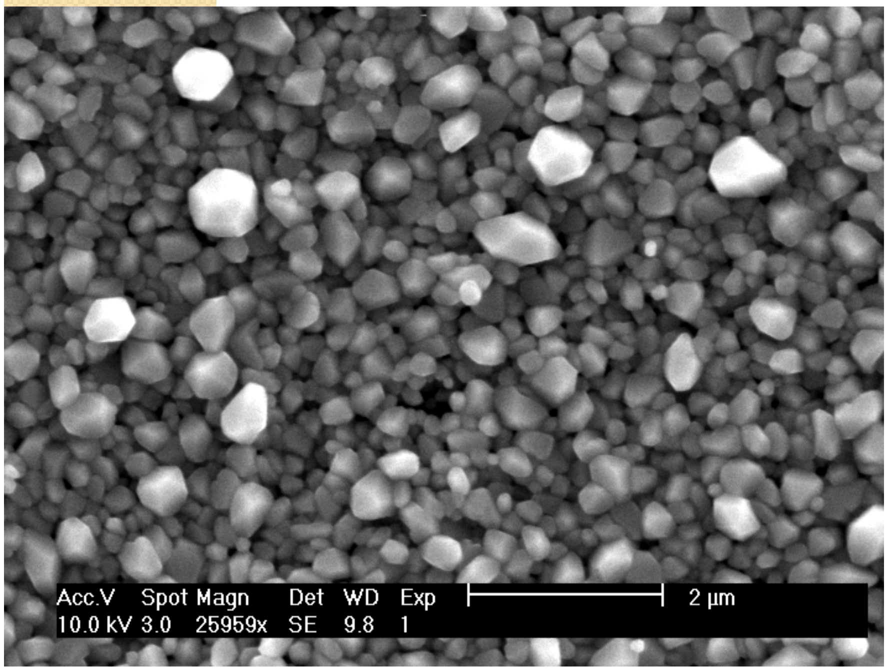
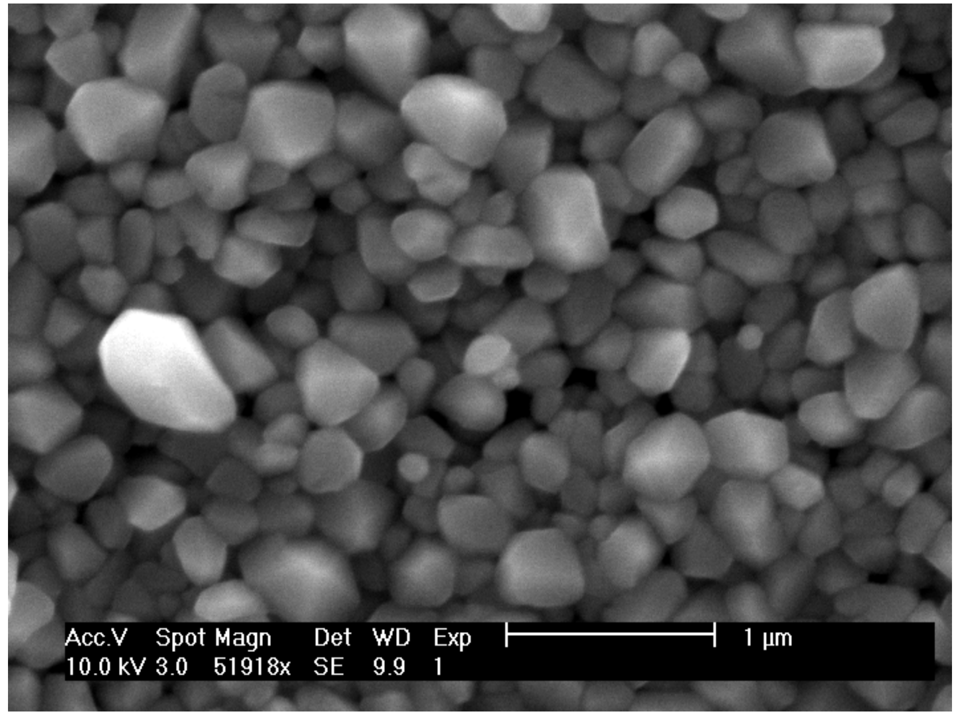

Acc.V Spot Magn Det WD Exp 5 µm
10.0 kV 3.0 7718x SE 9.8 1

15mg S, 550℃, 6hr, 7layers

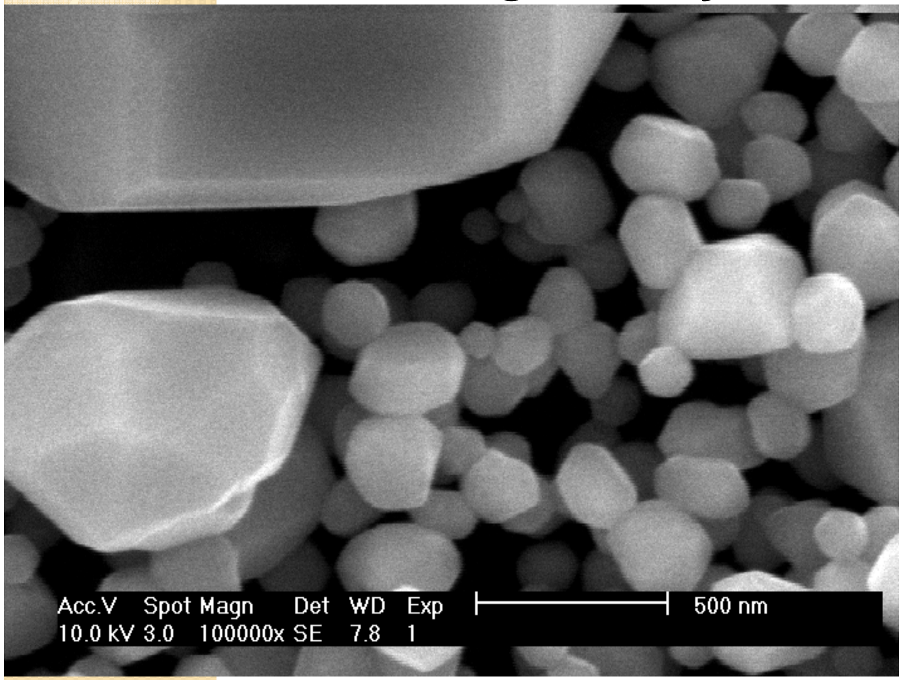


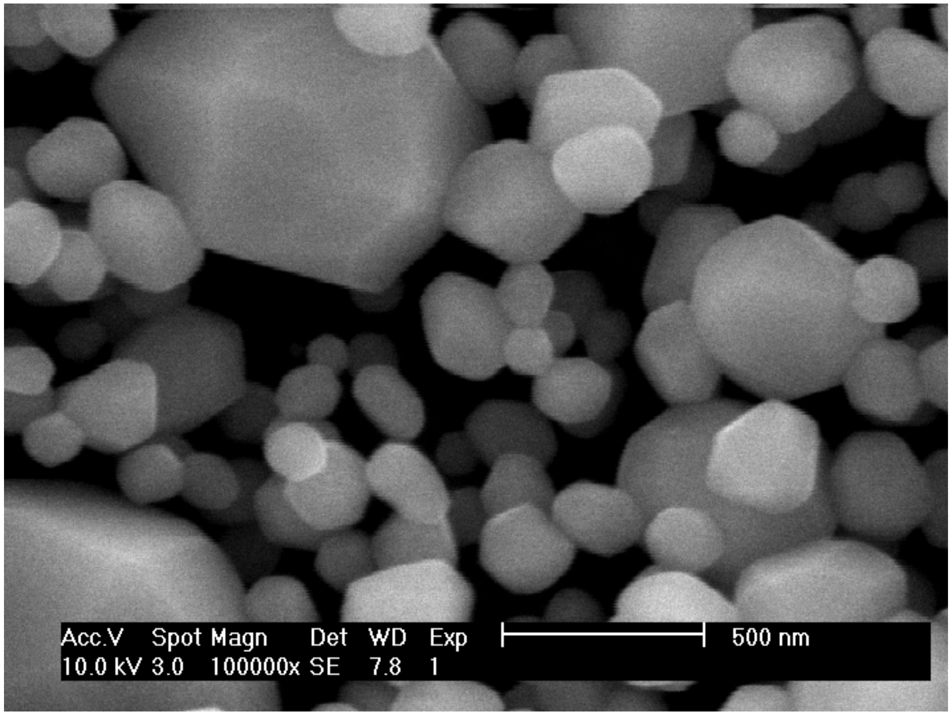


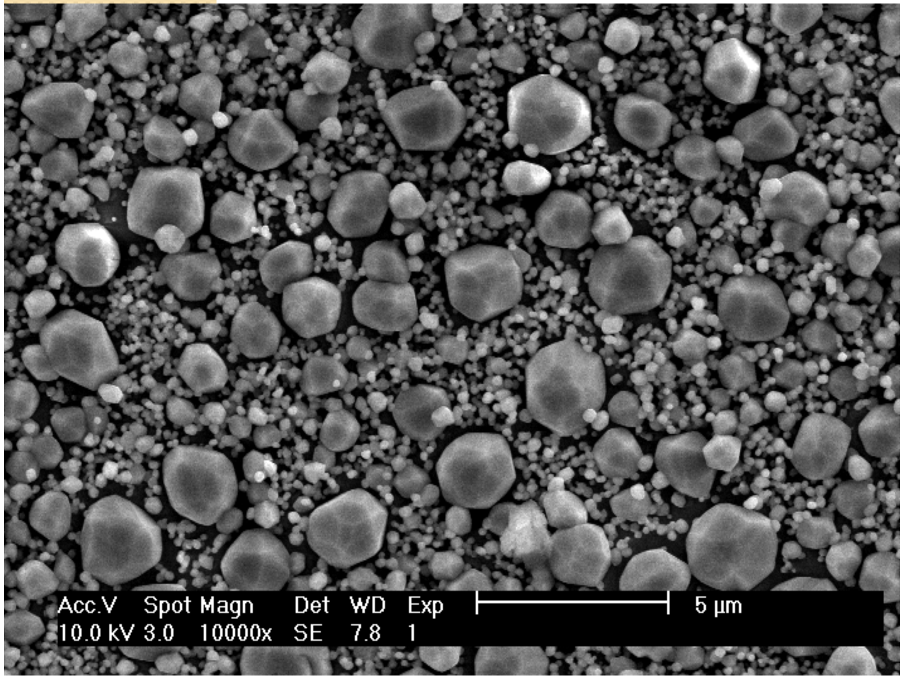


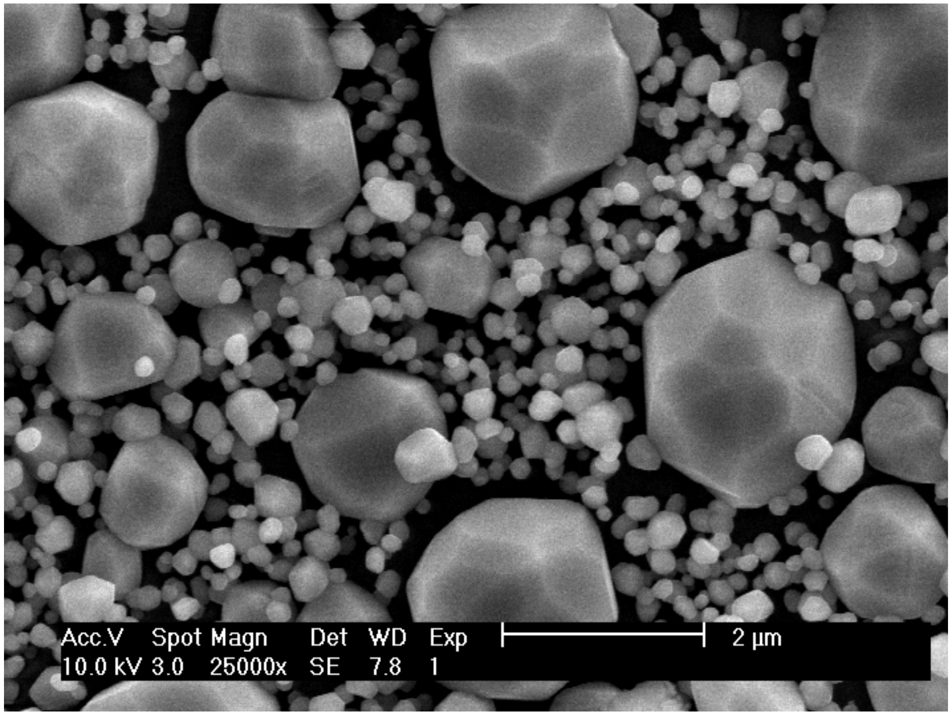


550 °C, 6hrs, 100 mg S, 7 layers









Future Work

- Determining chemical composition
  - Thermogravimetric Analysis
  - Differential Scanning Calorimetry
  - Mass Spectrometry
  - Powder X-Ray Diffraction
  - Nuclear Magnetic Resonance
  - XPS – look for contaminants (O, C, N, Na)
- S_2 annealing: vary S content, temperature, total cook time
- H_2S annealing: time, temperature
- Exchanging ethanolamine with ethylene glycol (less toxic)
- Alloying with Zn