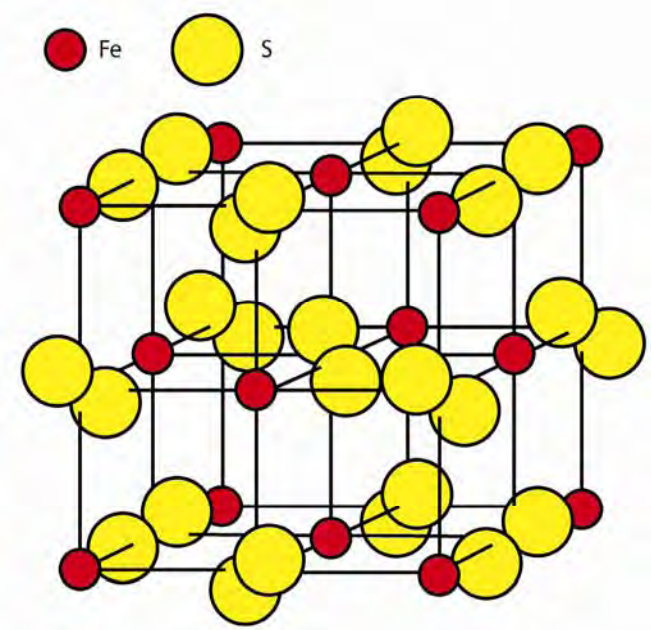
Iron Pyrite (FeS_2)

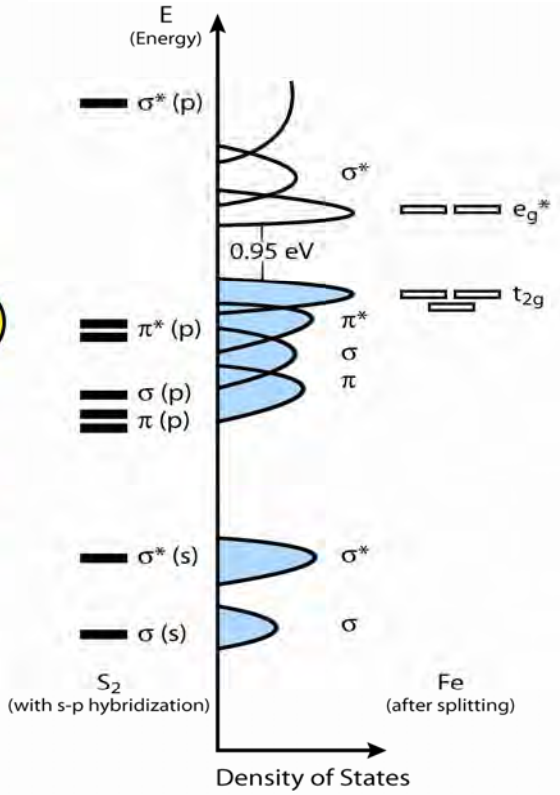
Fool's gold

- suitable bandgap (0.95 eV)
- very strong light absorption
- adequate diffusion lengths
- extremely cheap
- infinitely abundant

Crystal structure



Electronic structure

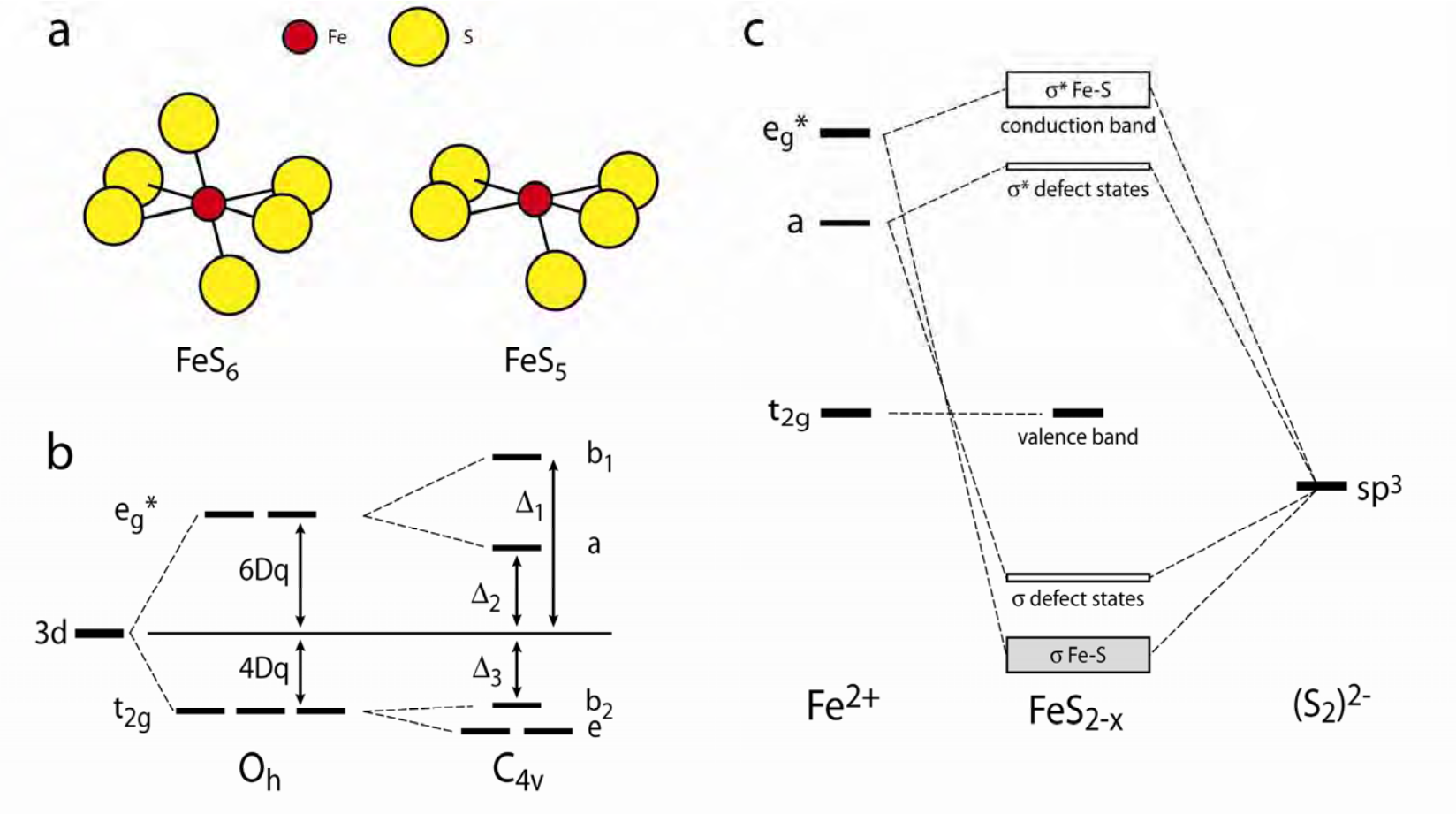


Pyrite tops a short list of thin film materials capable of scaling to multiple TWs without resource limitations

Pyrite suffers from a low voltage

Pyrite tends to be sulfur deficient, and sulfur defects create states in the bandgap, limiting the voltage

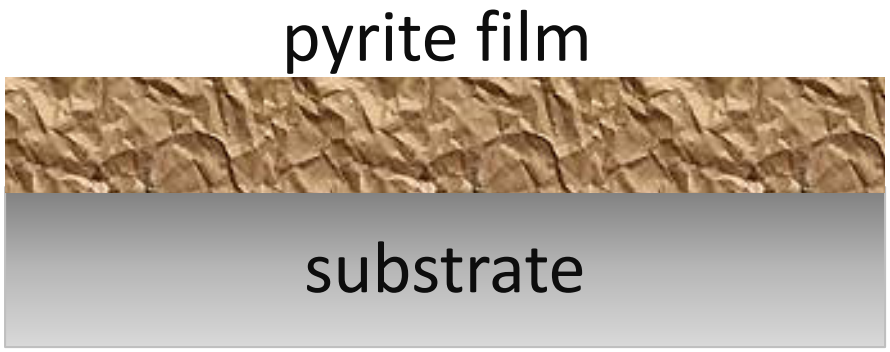
Performance: 40 mA cm^{-2} , < 0.2 V, 3.3%



Passivating surface defects is the key to boosting cell efficiency

Pyrite growth update

Our goal: **Powerpoint Perfect Pyrite**



- uniform, dense, pinhole free
- largest possible grains
- tunable thickness (50–2000 nm)
- flat
- stoichiometric
- scalable processing
- substrate independent

Team Pyrite

Nick – CVD

James – nanocrystal inks

Sean – NC & molecular inks

Krys – CdS CBD

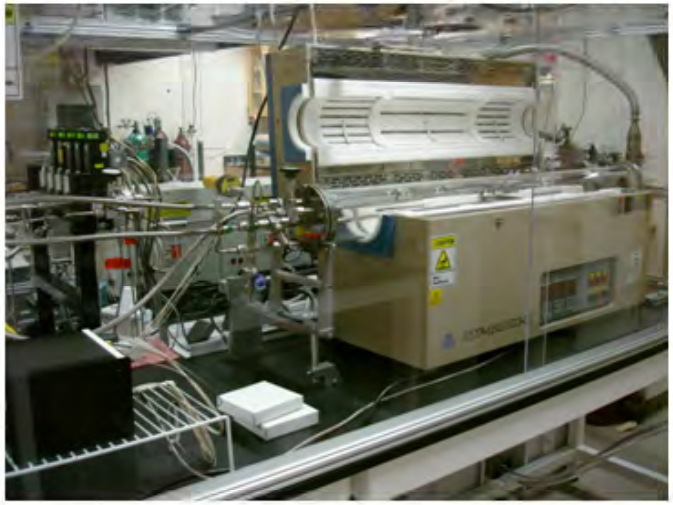
Amanda – molecular inks

Yinglei – ZnS CBD

Pyrite growth capabilities

1” hot wall CVD

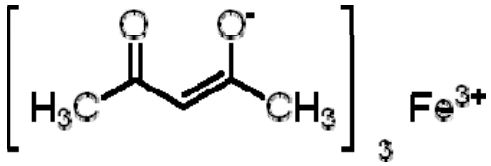
5” cold wall CVD



sulfur annealing furnaces

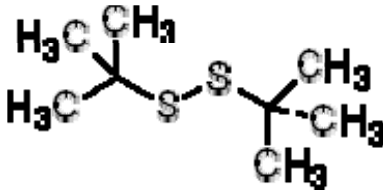
4” H_2S/H_2 annealing system

Chemical vapor deposition (CVD) route

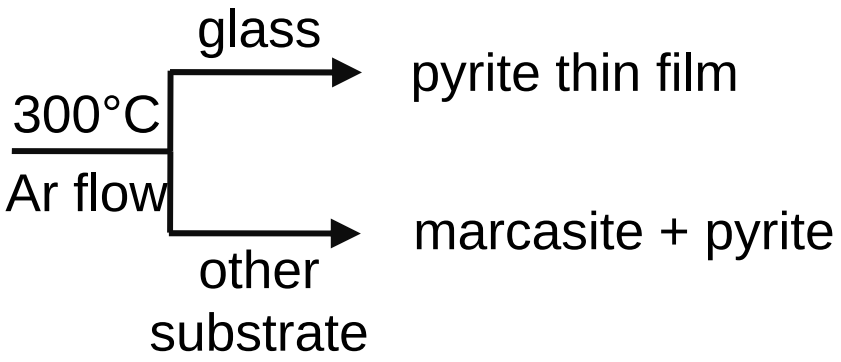


$Fe(acac)_3$ (solid)

+

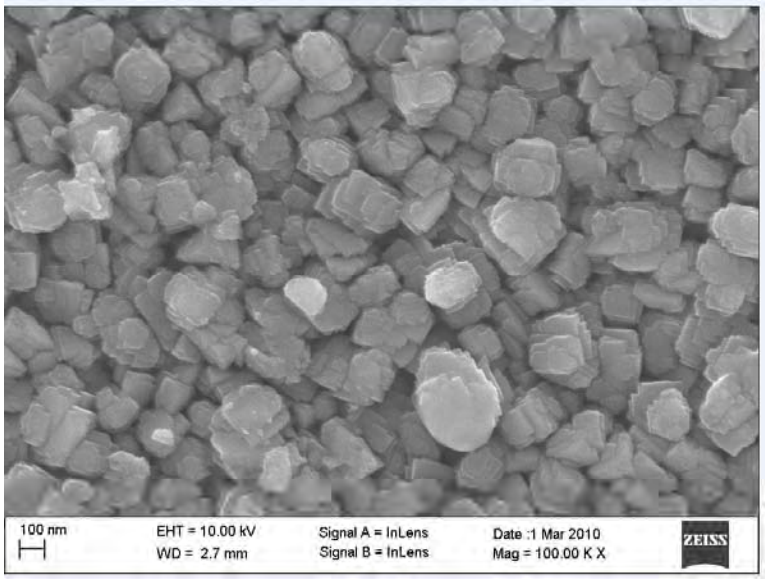


TBDS (liquid)

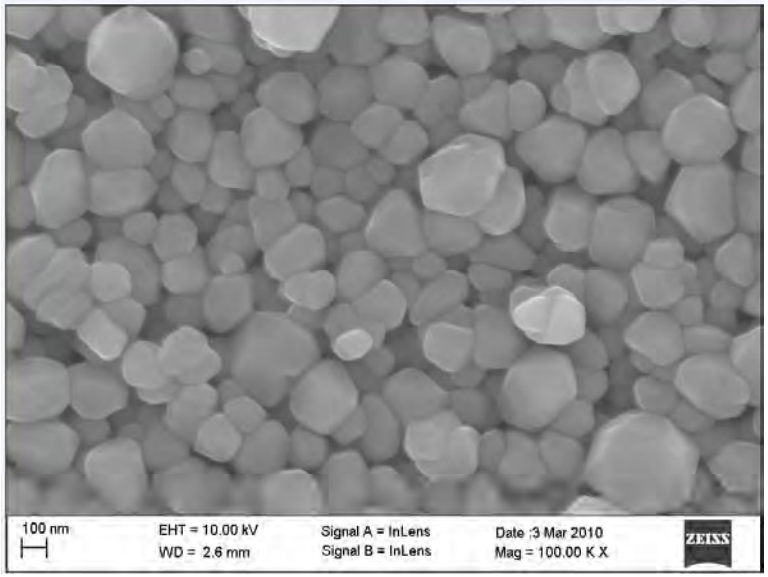


Films are annealed in S_2 to convert marcasite to pyrite and improve grain structure.

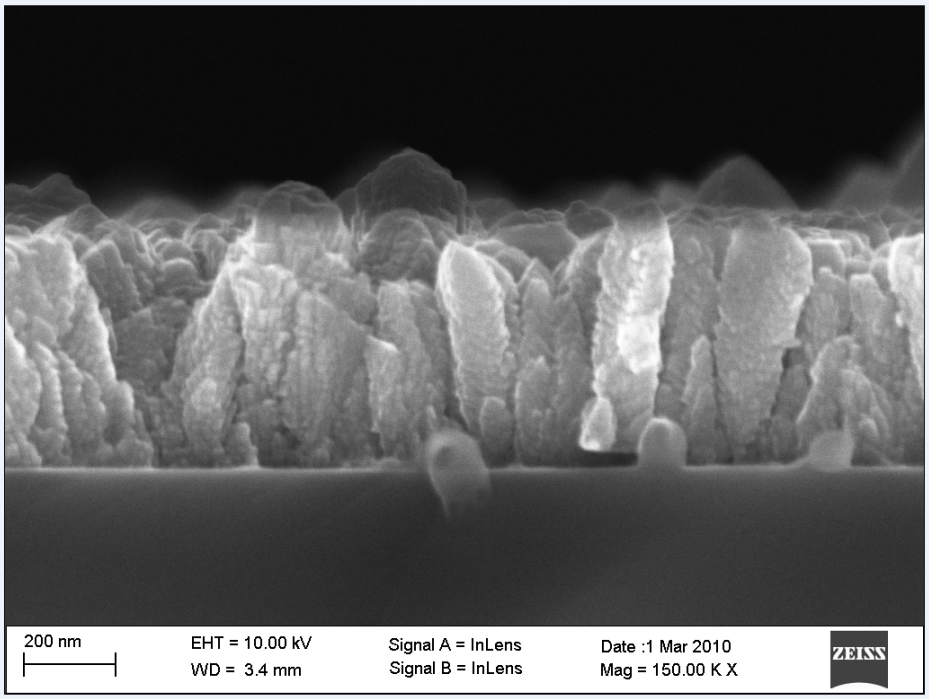
on glass (pure pyrite)

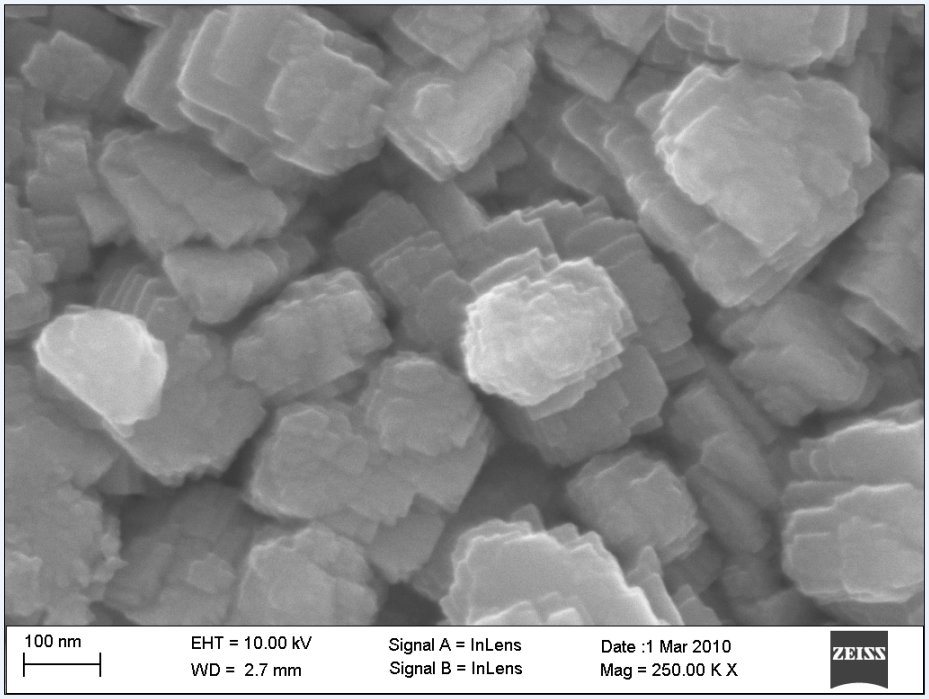


500°C S_2 annealed (pure pyrite)

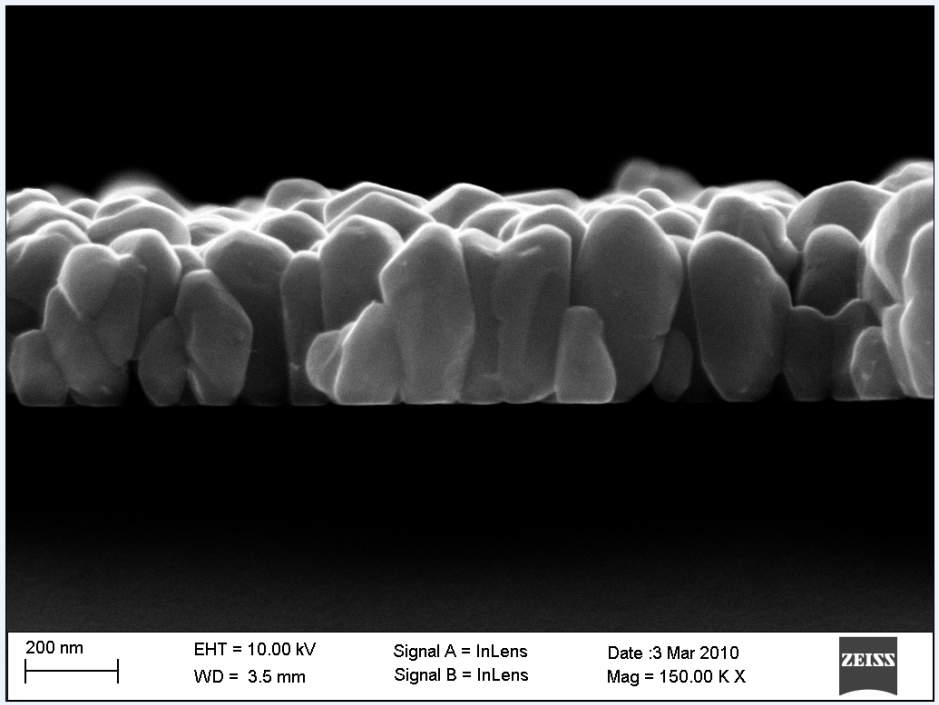


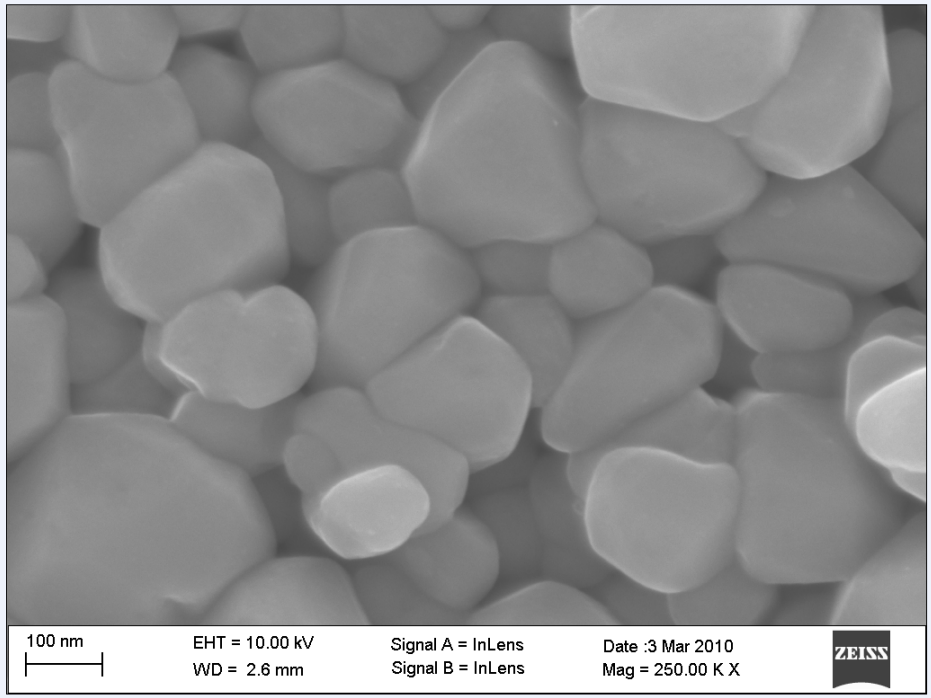
on **glass** (pure pyrite)



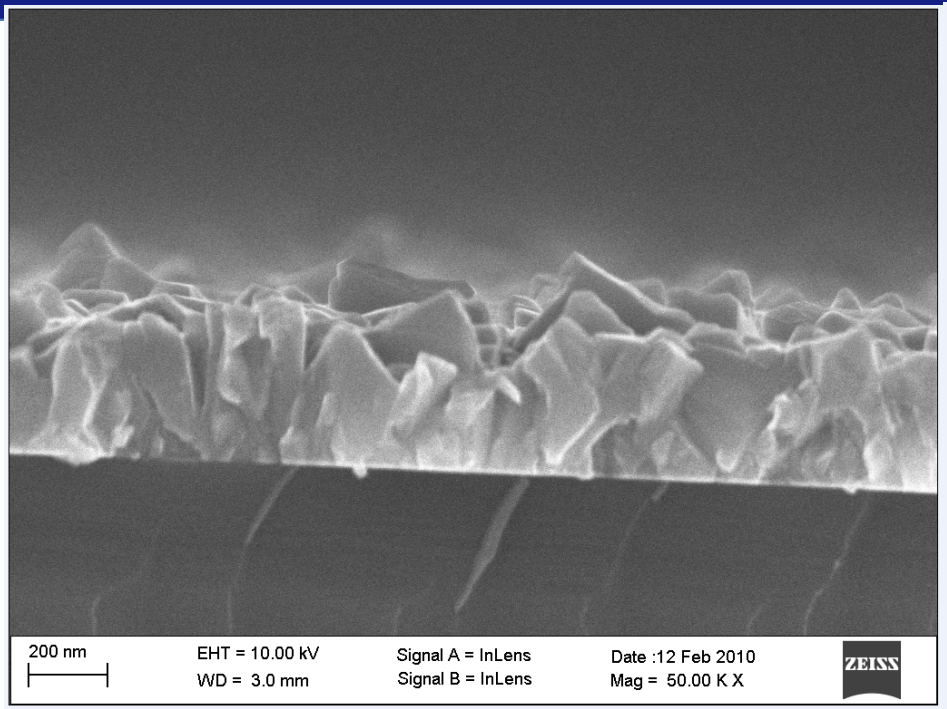


500°C S_2 annealed (pure pyrite)

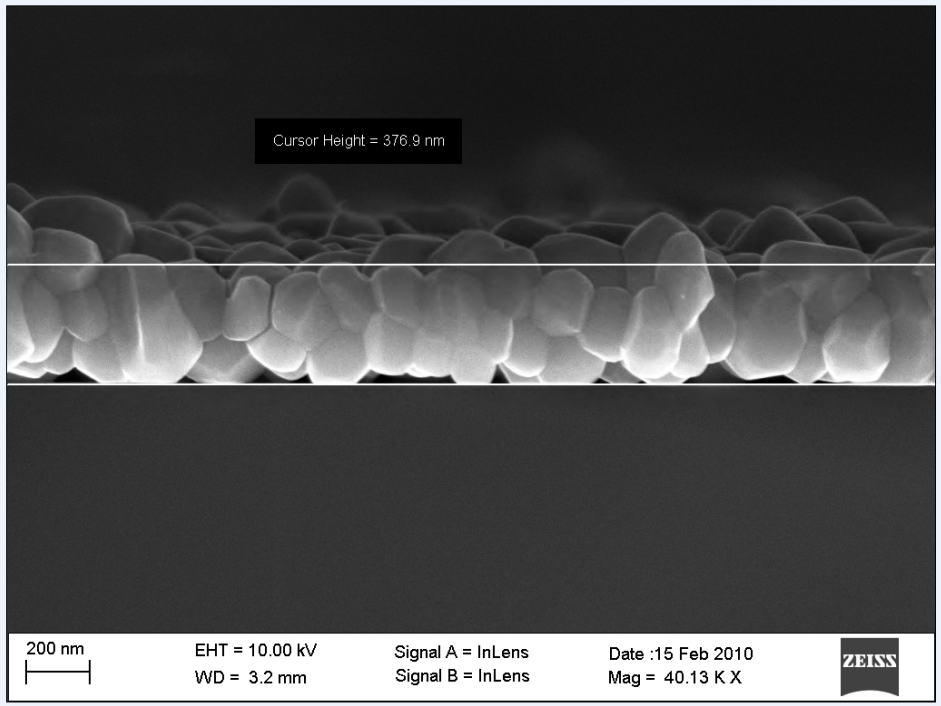


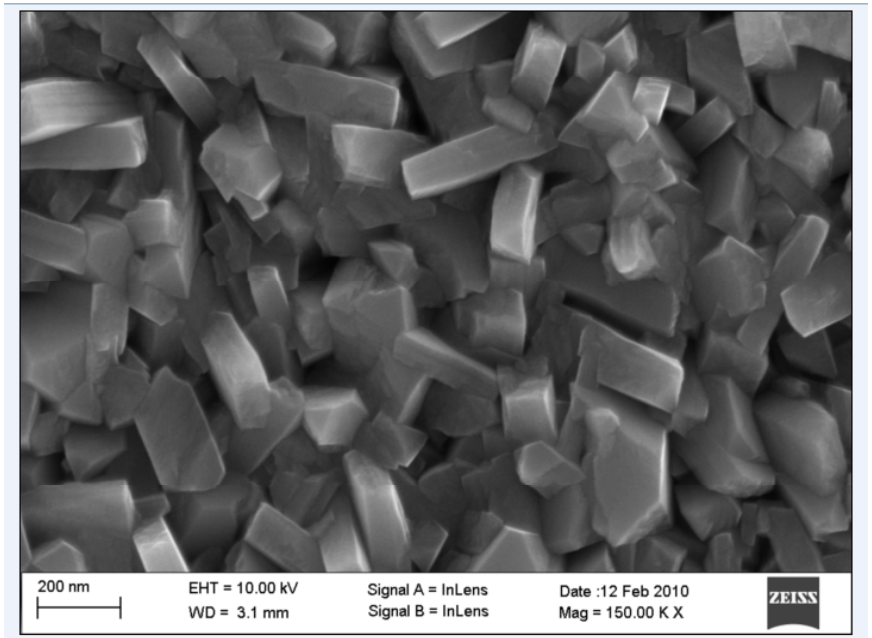


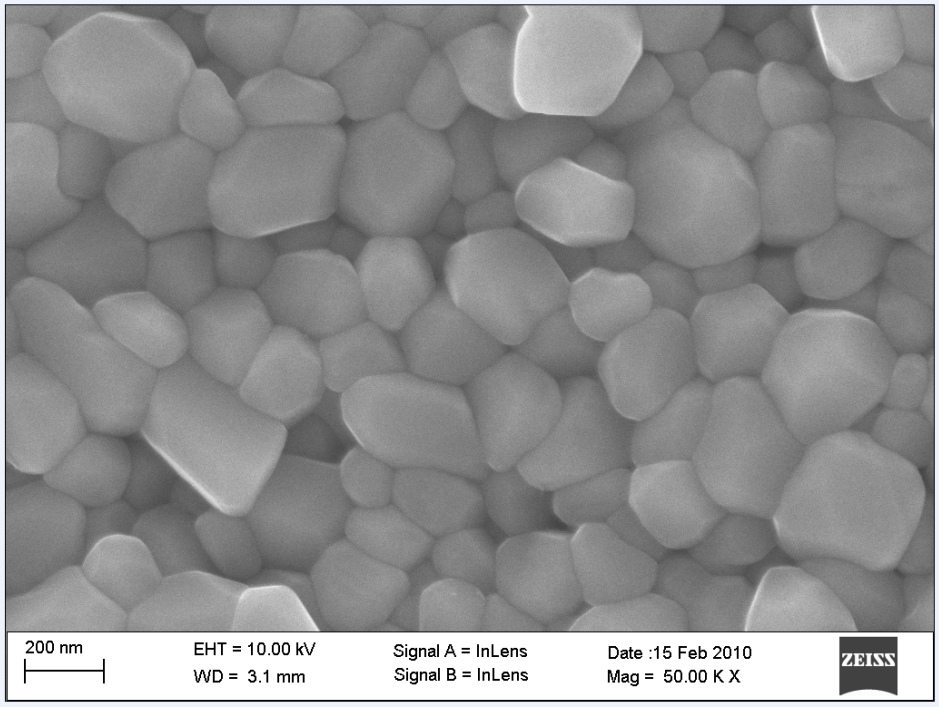
on **silicon** (marcasite/pyrite)



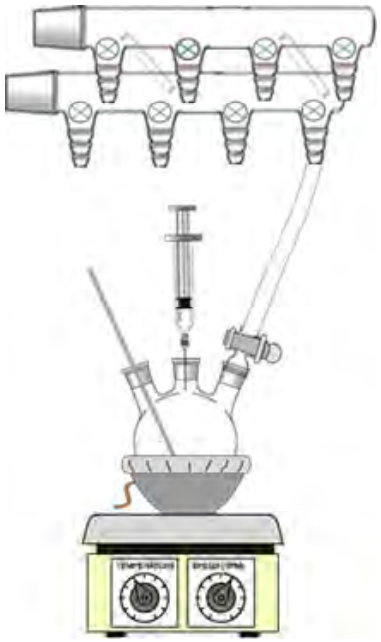
650°C S_2 annealed (pure pyrite)





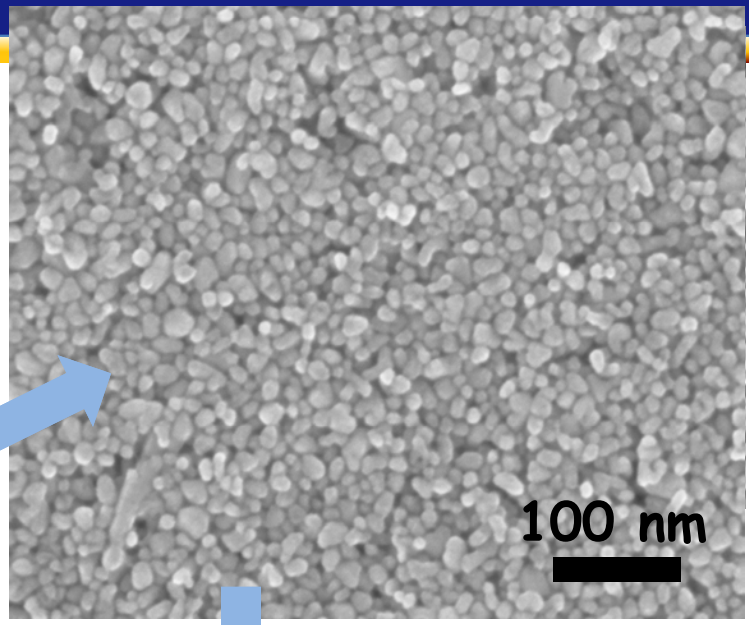


Nanocrystal approach (James, Sean)

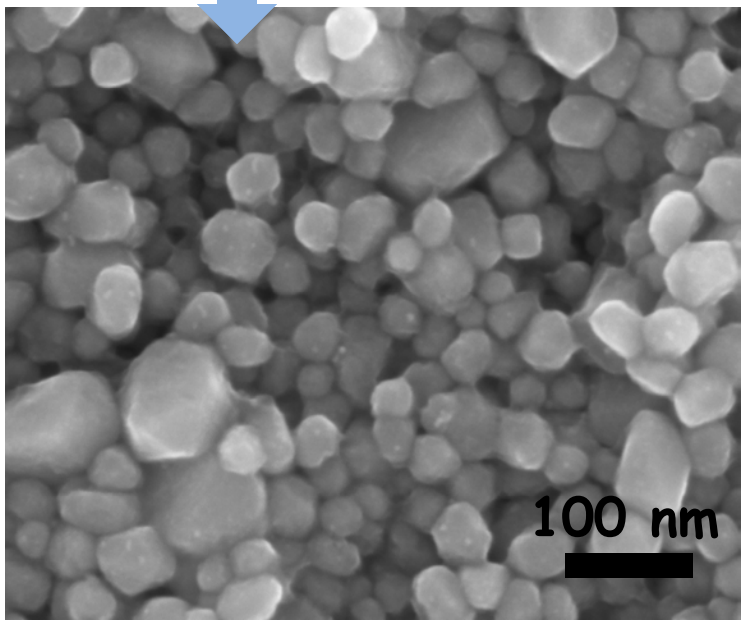


Synthesize NCs

Dip coat to make NC film

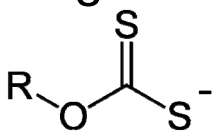


Sinter in sulfur



Procedure

- $FeCl_2$ + sulfur in octadecylamine at 220°C.
- Ligand exchange to octadecylxanthate to improve solubility.

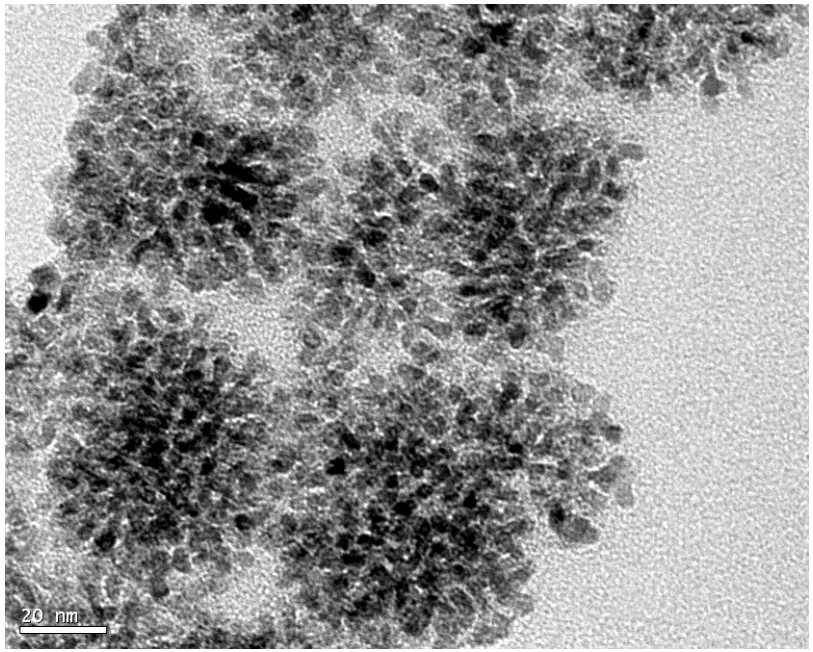


- Dip coating in glove box (up to 3 um thick) from NCs in chloroform and 1 M hydrazine in CH_3CN
- Final anneal at 500-600°C in sulfur-filled ampoule.

Pyrite nanocrystals: A challenge

- multiple Fe-S phases
- difficult to crystallize
- tends to aggregate

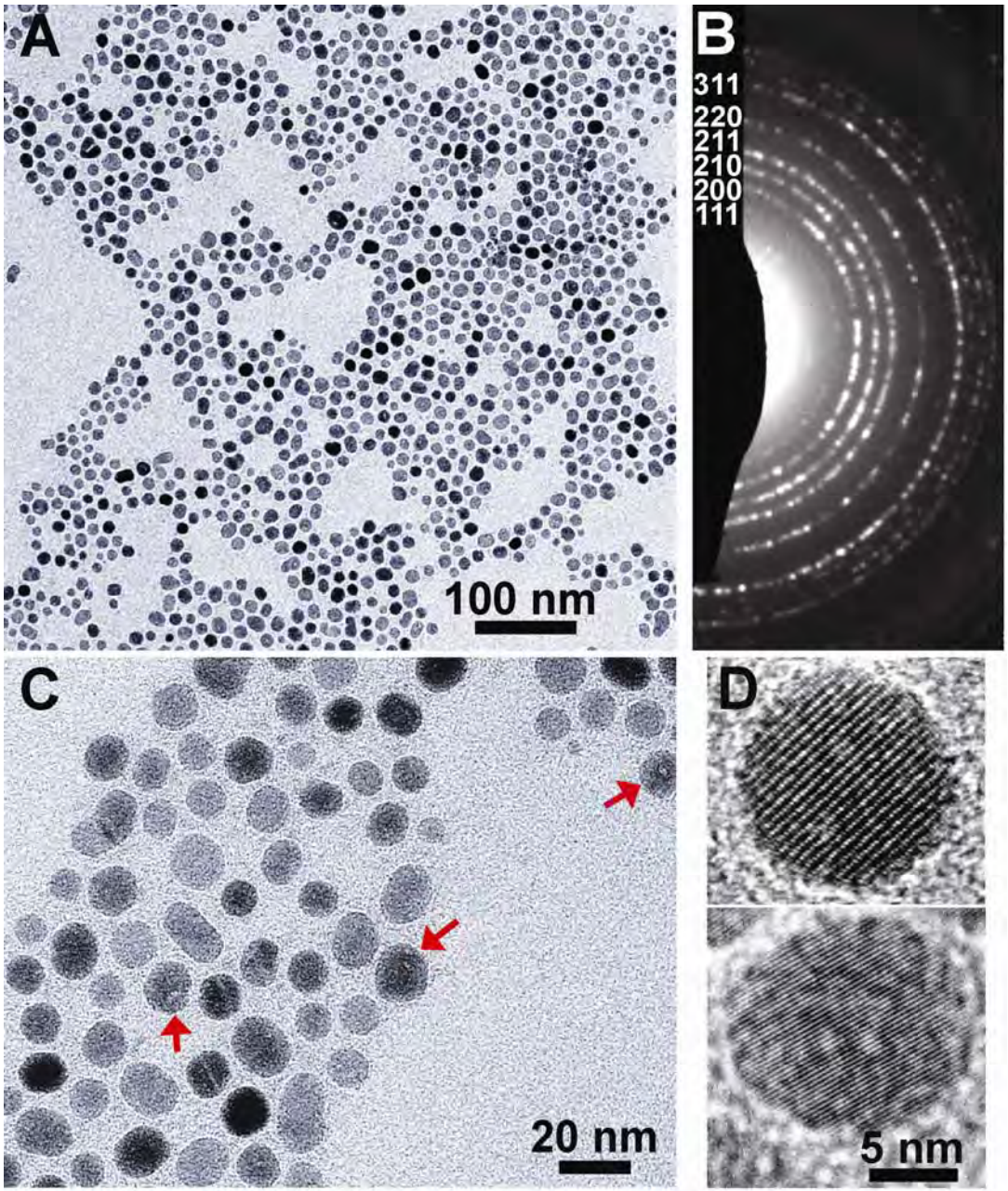
Early results: aggregates

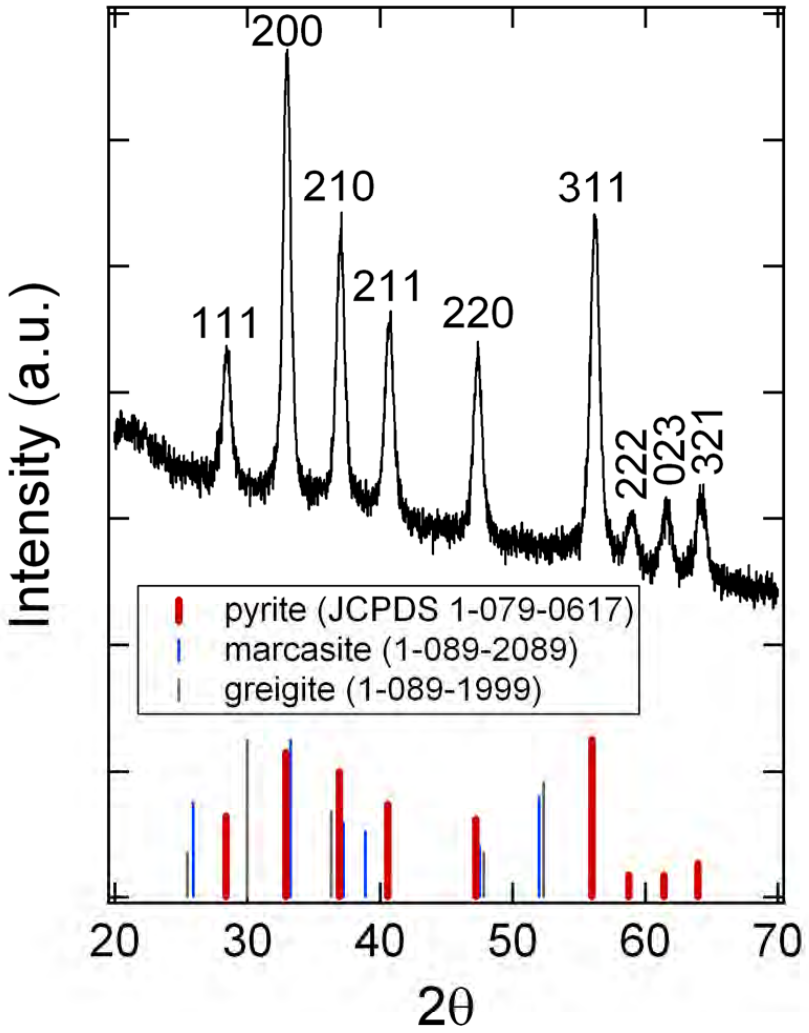


Iron sulfide phases

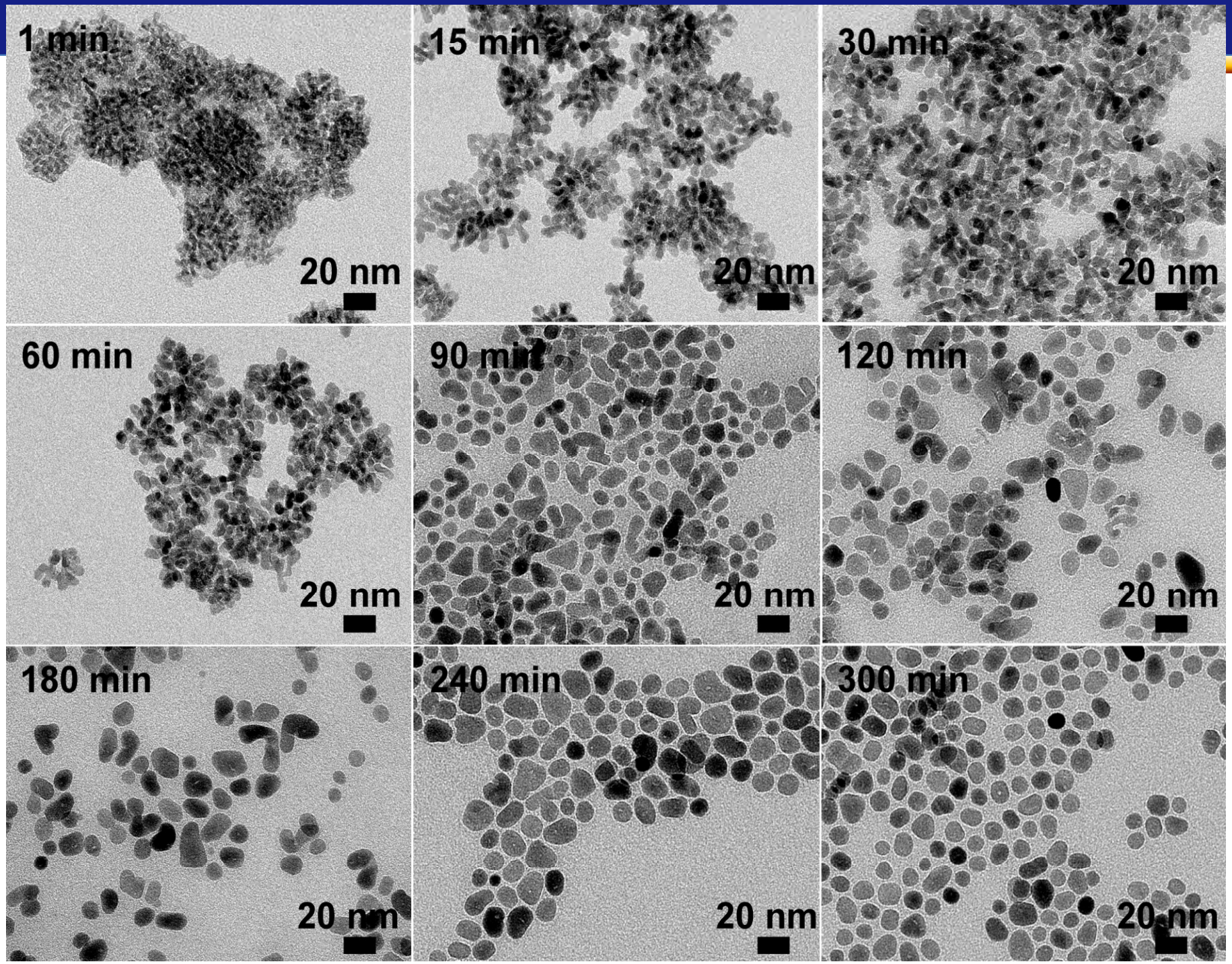
Pyrite (FeS_2)	cubic, E_g = 0.95 eV (indirect; 1.01 eV direct gap) diamagnetic semiconductor (Van Vleck paramagnet)
Marcasite (FeS_2)	orthorhombic, E_g = 0.4 eV (indirect) diamagnetic semiconductor
Greigite (Fe_3S_4)	cubic, E_g = 0.4 eV, ferrimagnetic
Pyrrhotite ($Fe_{1-x}S$, with $x \leq 0.2$)	hexagonal or monoclinic, $E_g \approx 0.2$ eV diamagnetic or ferromagnetic semiconductor
Troilite (FeS)	hexagonal, E_g = 0.04 eV, antiferromagnetic semiconductor

Pyrite nanocrystal inks



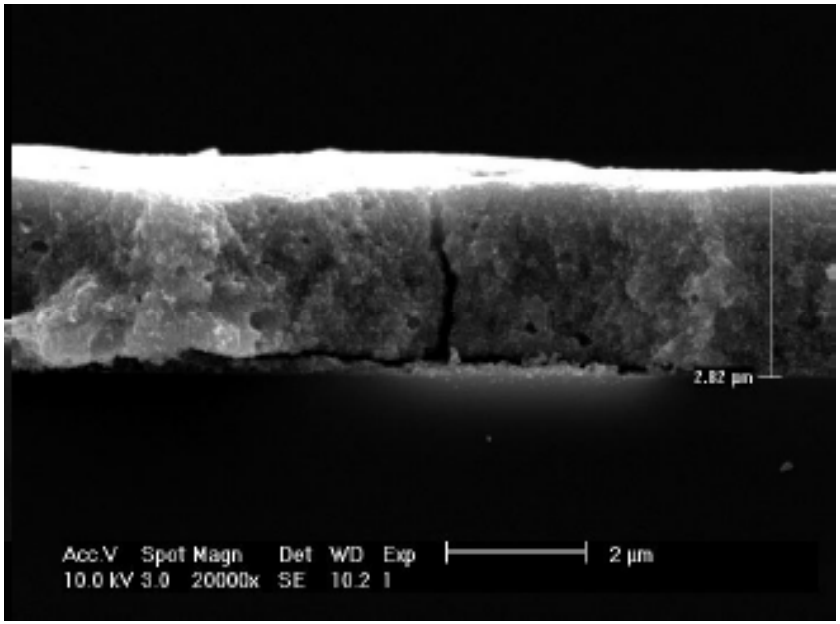


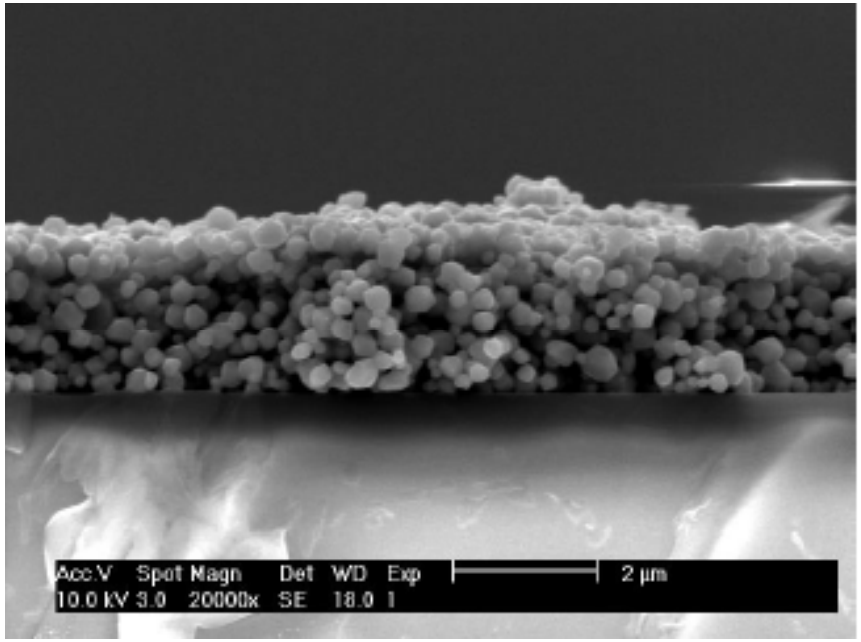
Reaction progression



Film formation

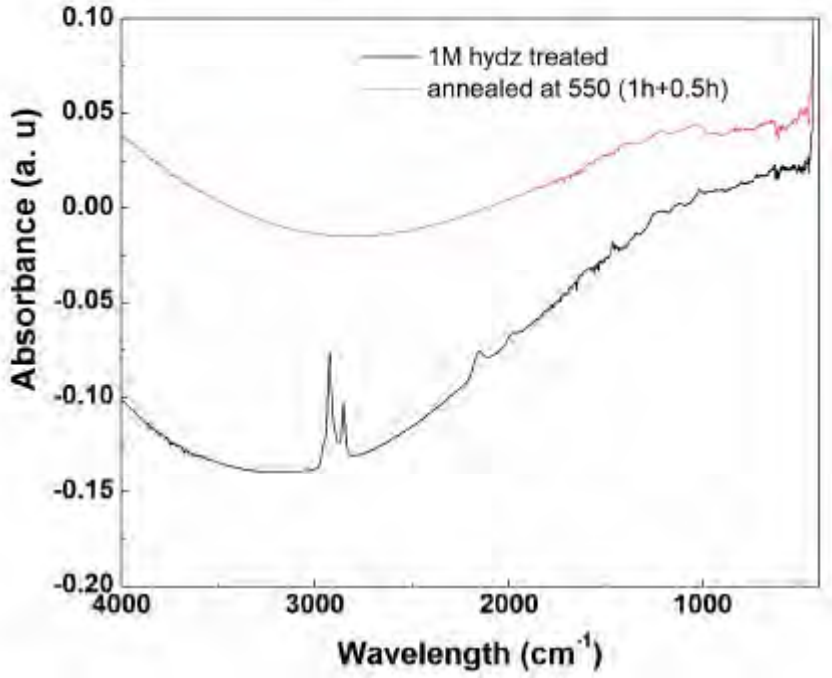
50 mg of sulfur, at 540 C, 4h annealing, rapid heating and cooling





Grain growth depends on:

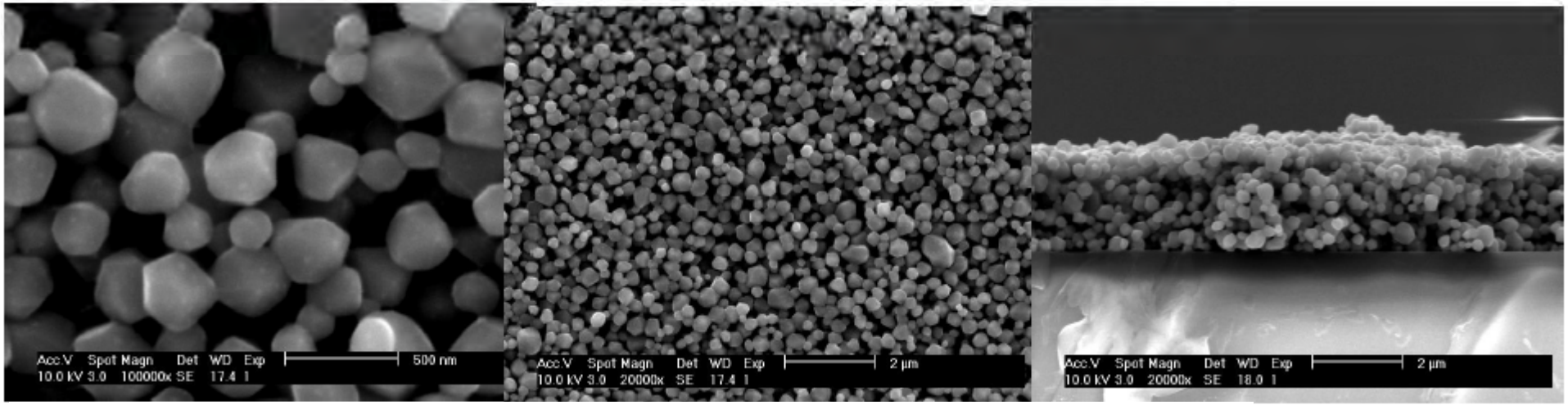
- temperature
- time
- heating/cooling rates
- substrate
- amount of sulfur



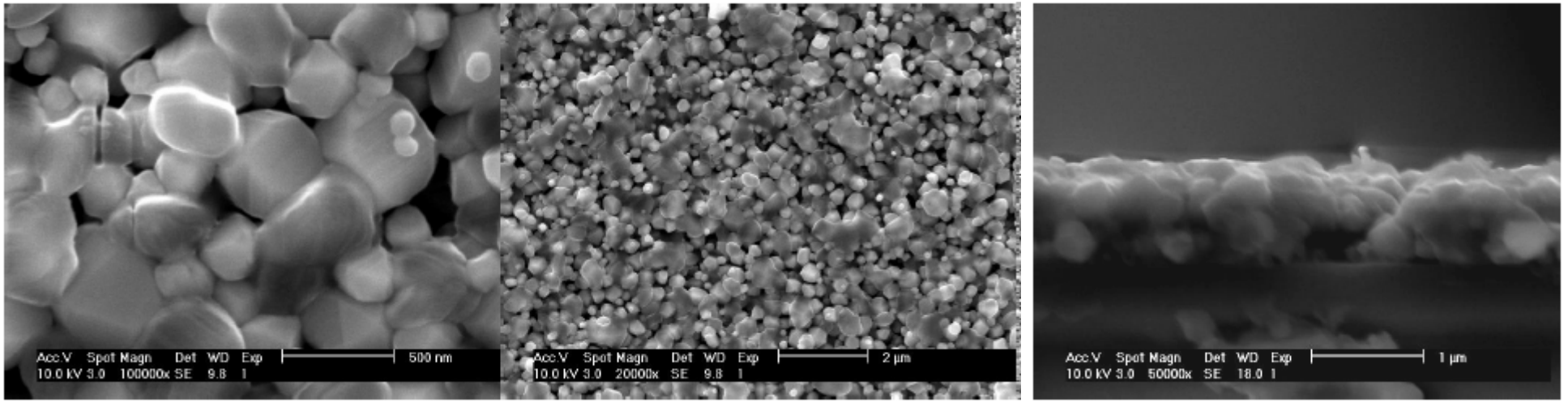
On glass

Pyrite nanocrystals on glass showed better quality grains in terms of distribution and size

b) With 50 mg of sulfur, at 540 C, 4h annealing, rapid heating and cooling



With 100 mg of sulfur, 540 C, 4h annealing, contolled heating and cooling



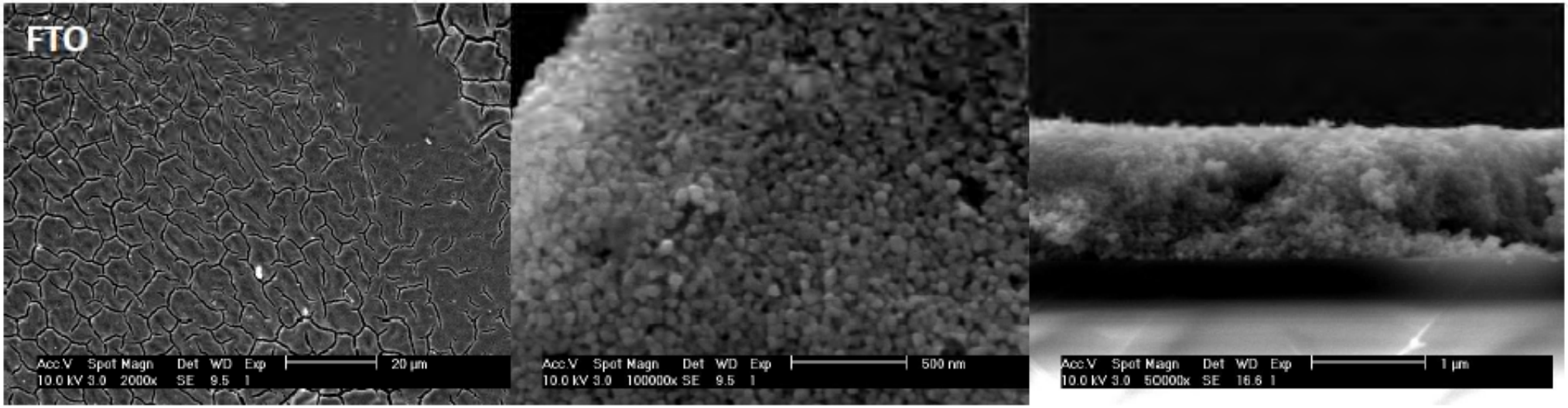
Controlled cooling instead of natural cooling resulted in better connected grains

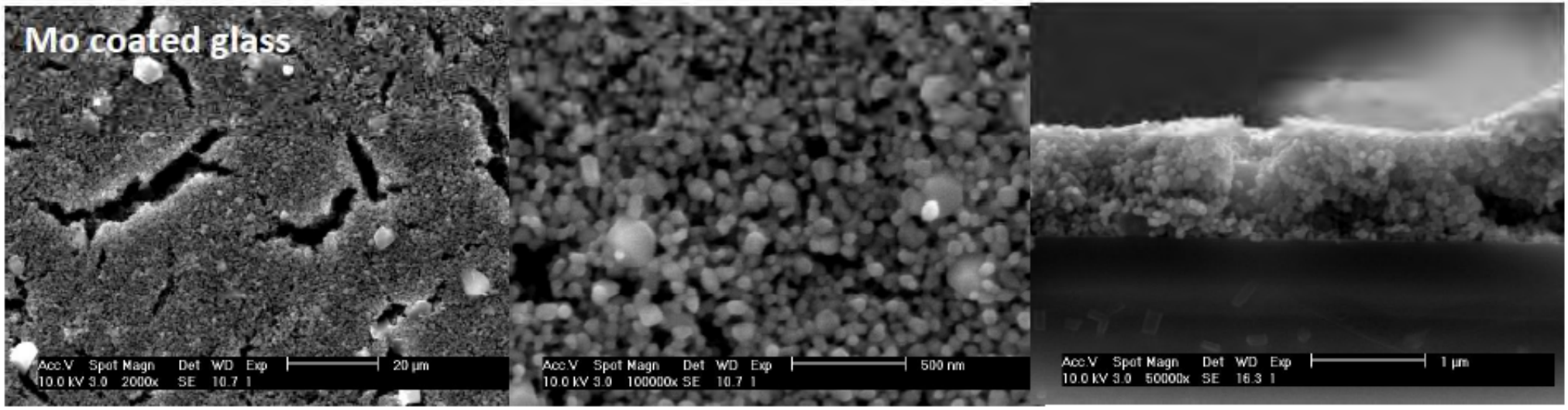
Attempts to yield well connected grains are continuing

On potential device substrates

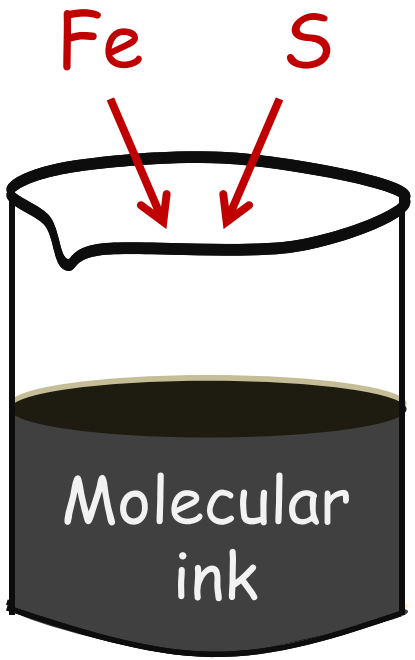
On different substrates

500 C, 4h cooking

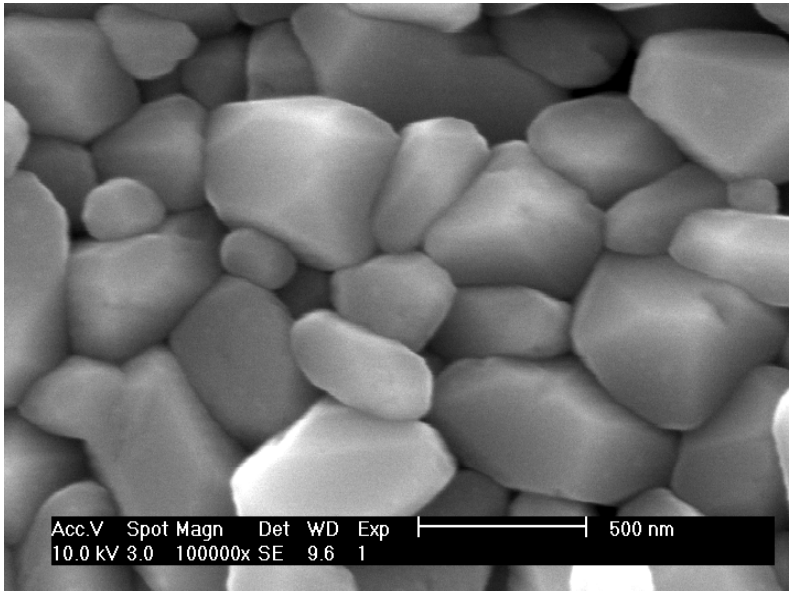




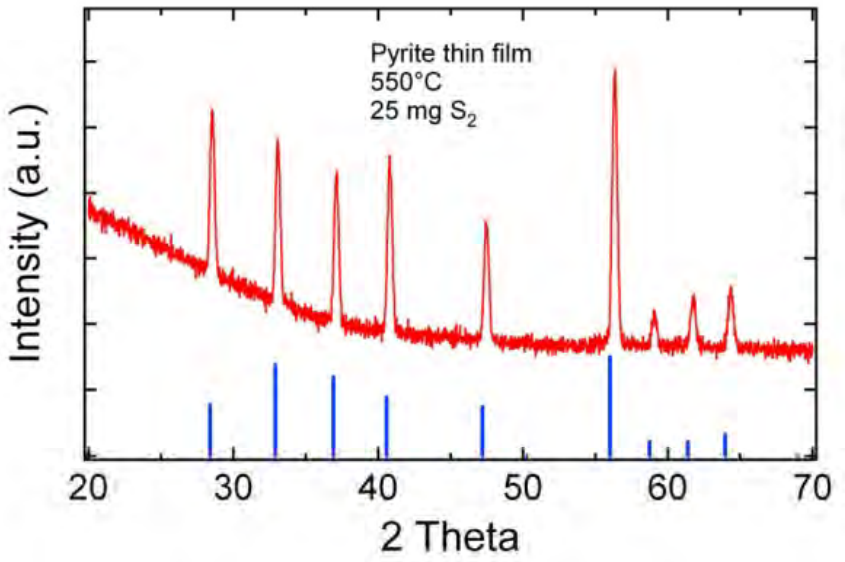
Molecular ink approaches



cast & cook



- simple and scalable
- low/no impurities
- tunable composition
- easy doping/alloying
- low toxicity



Molecular ink approach #1

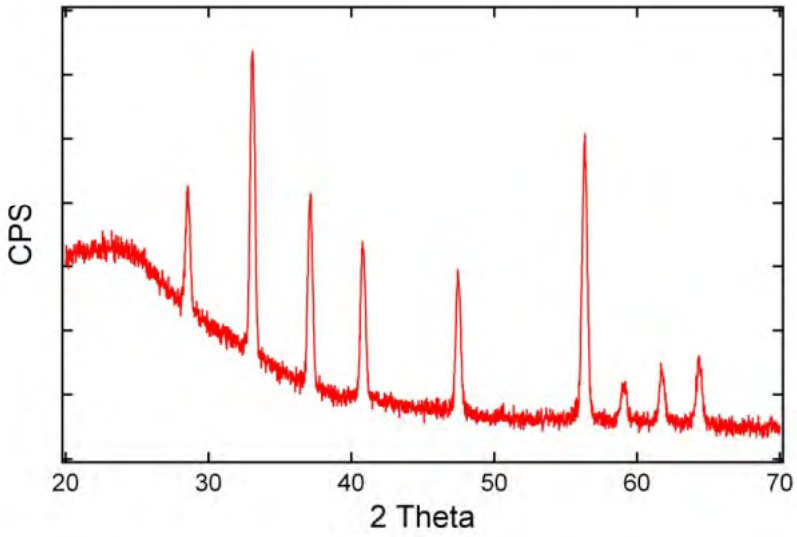
1. $Fe(acac)_3$ route (Sean)

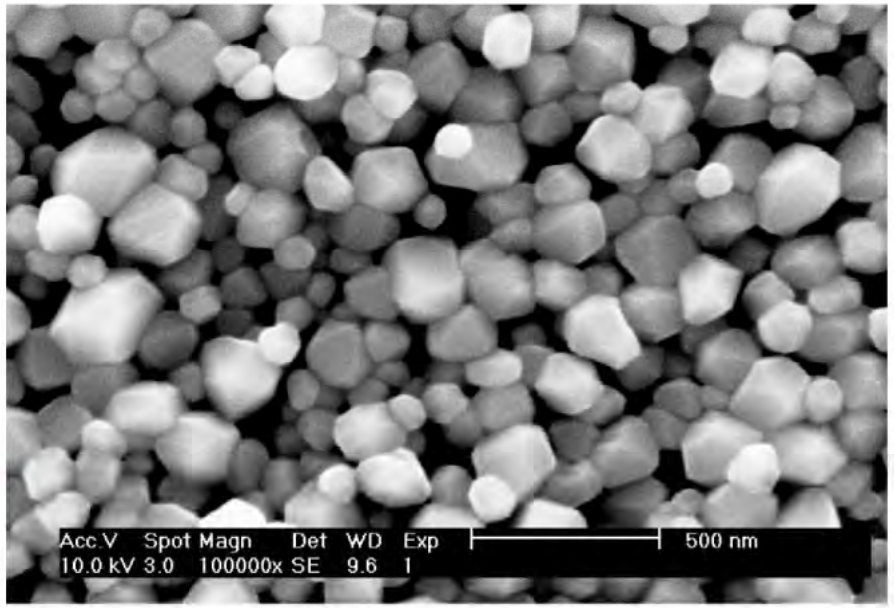
Procedure

- 0.8 M $Fe(acac)_3$ + 1.2 M sulfur in pyridine.
- Spin coat 200 nm layers, with 350°C bake in between each layer.
- Final anneal at ~550°C in sulfur-filled ampoule.

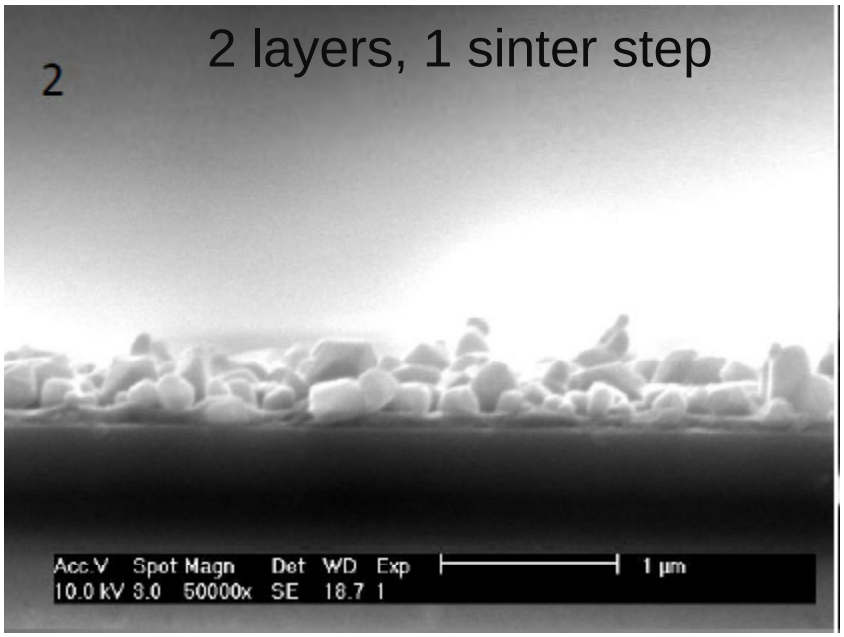
Progress

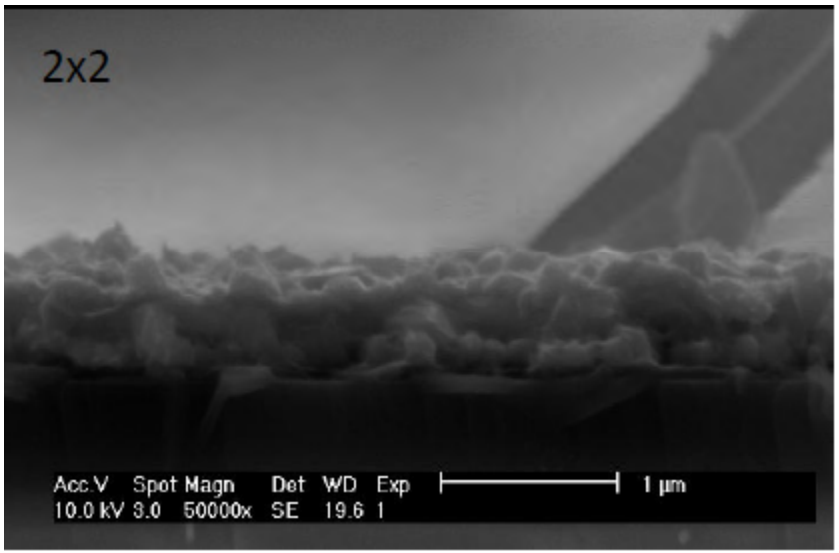
- single-anneal films show unconnected grains
- “2 + 2” process gives moderately dense, medium grain films (rough top layer)

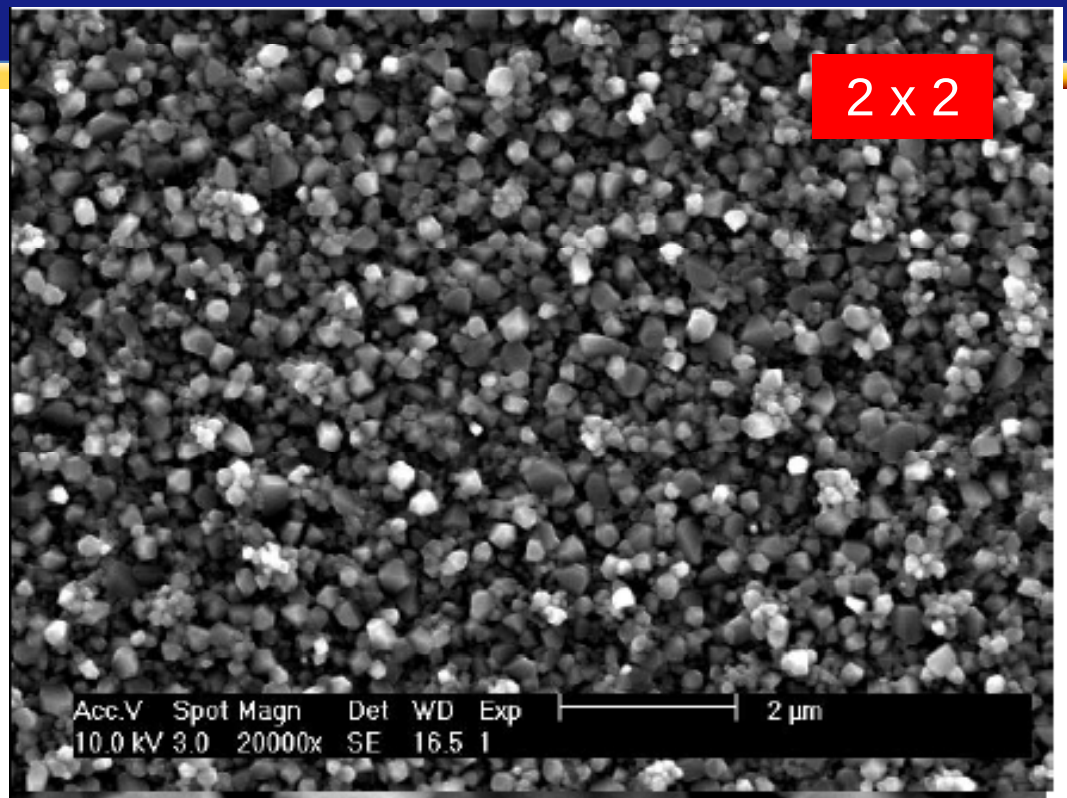


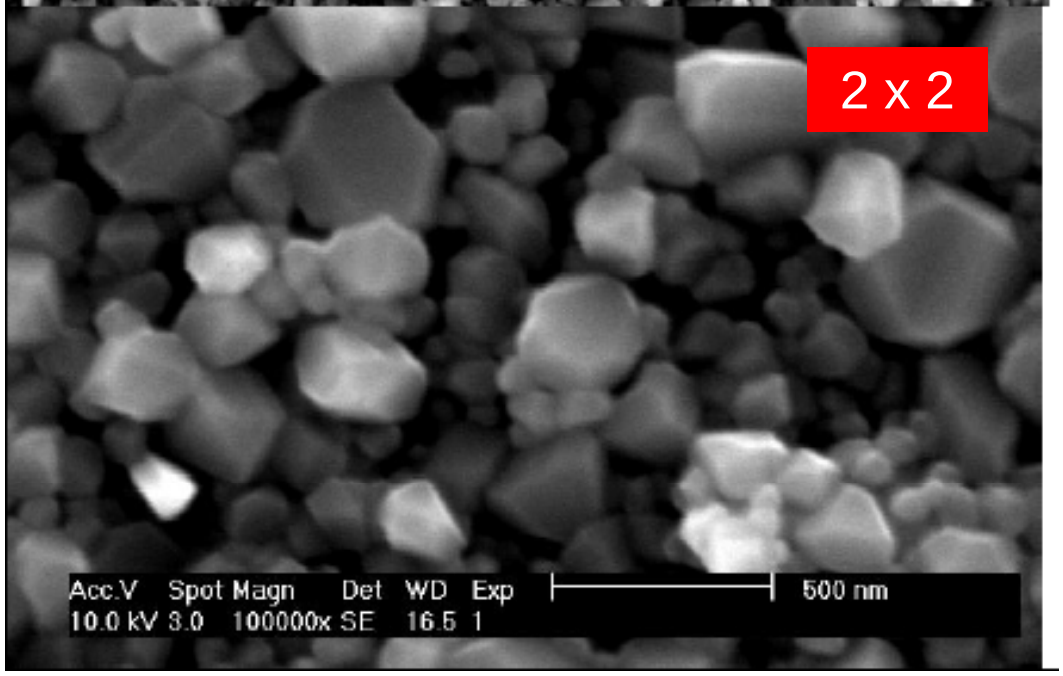


On glass substrates



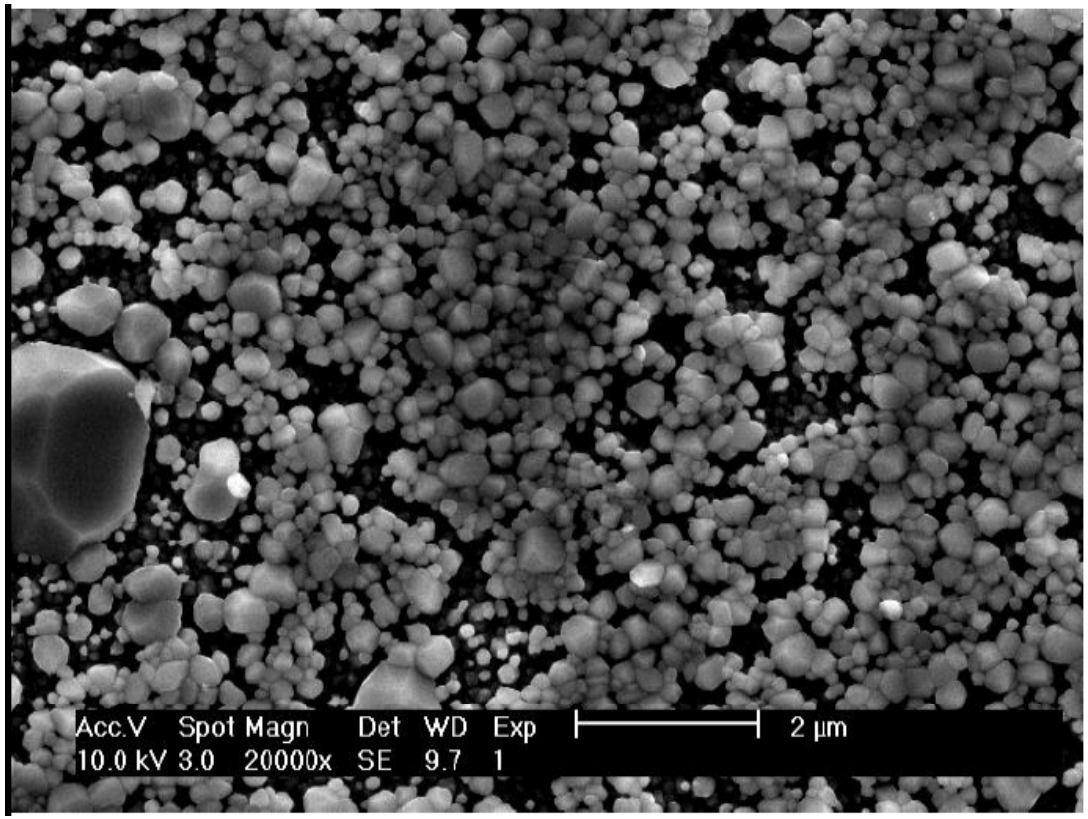


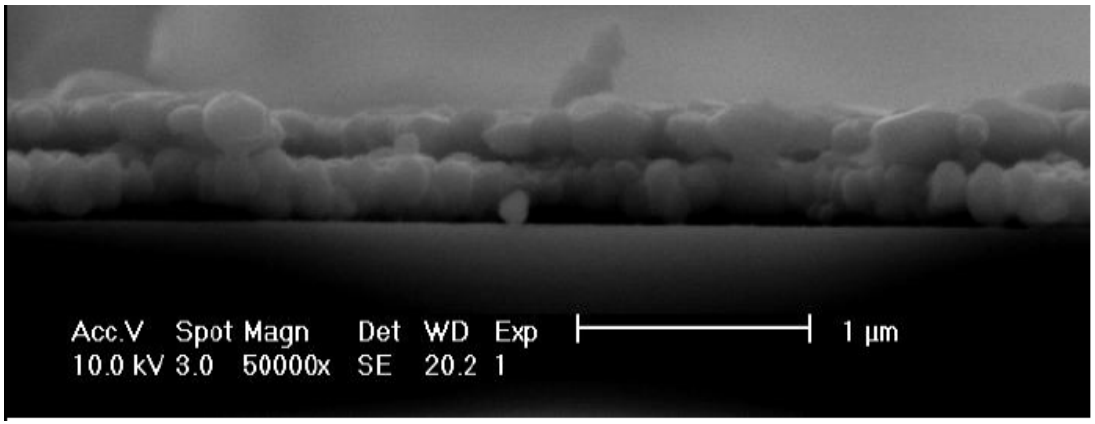




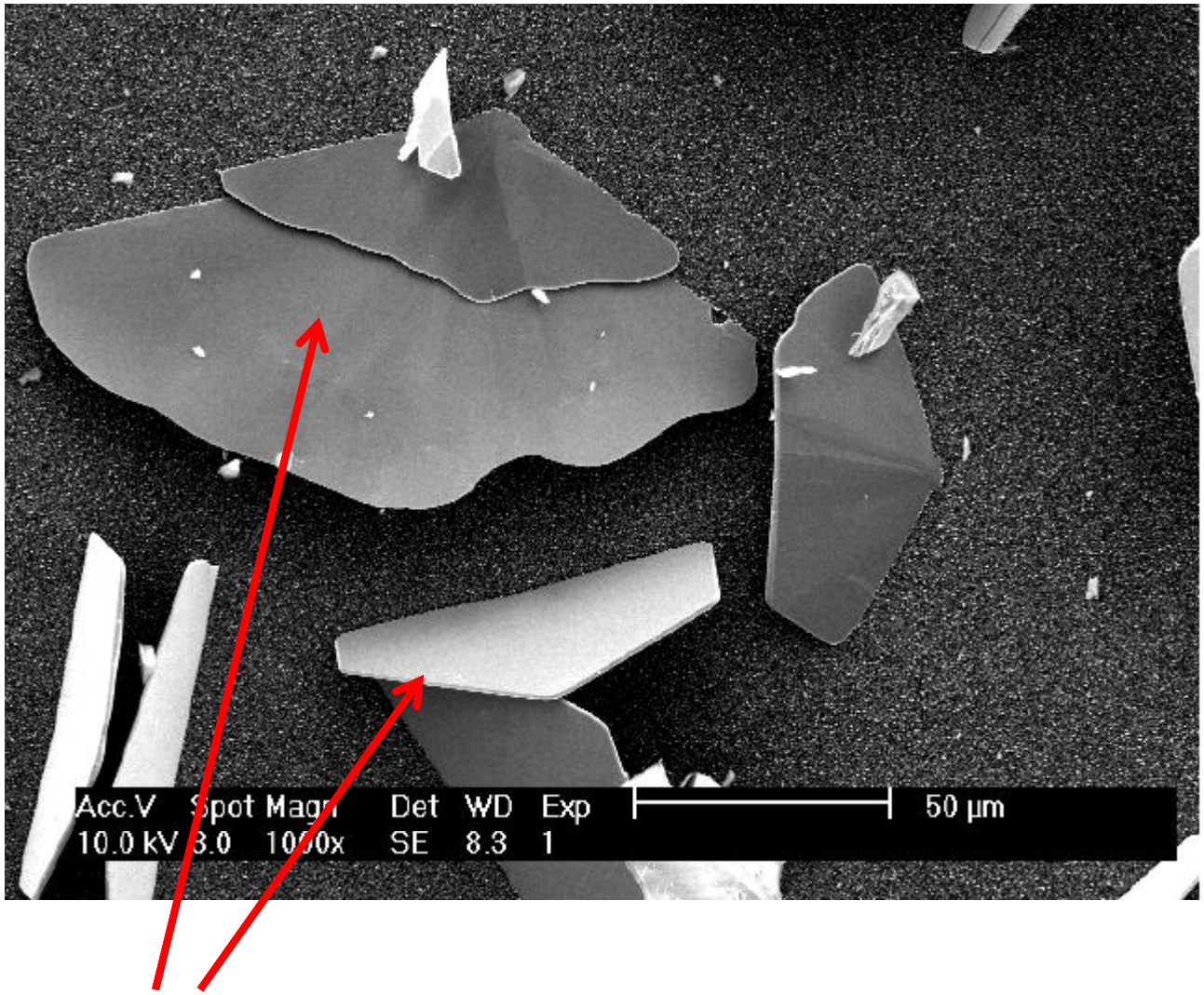
On quartz substrates

"2 + 2" process
350°C bakes in air
650°C S_2 anneal





Growth on FTO



hexagonal SnS_2 plates form on F:SnO_2

Molecular ink approach #2

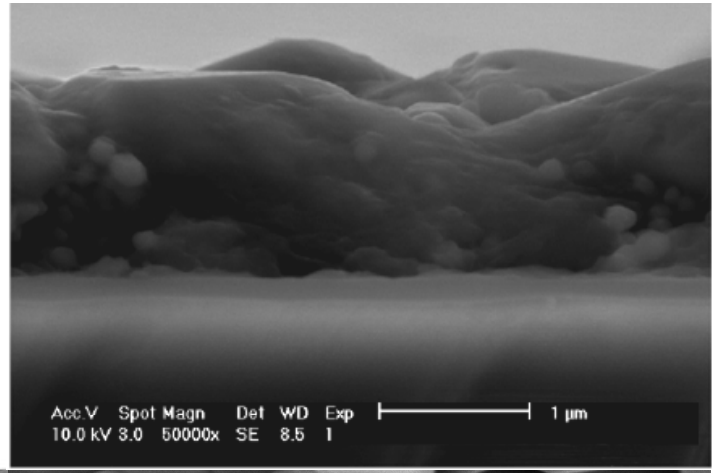
2. Iron route (Amanda)

Procedure

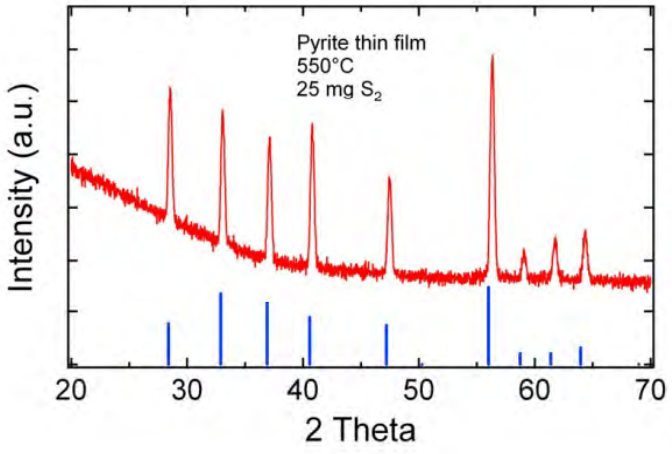
- Fe + sulfur in DMSO/ethanolamine.
- Spin coat ~150 nm layers, with 200°C bake in between each layer.
- Final anneal at 400-600°C in sulfur-filled ampoule.

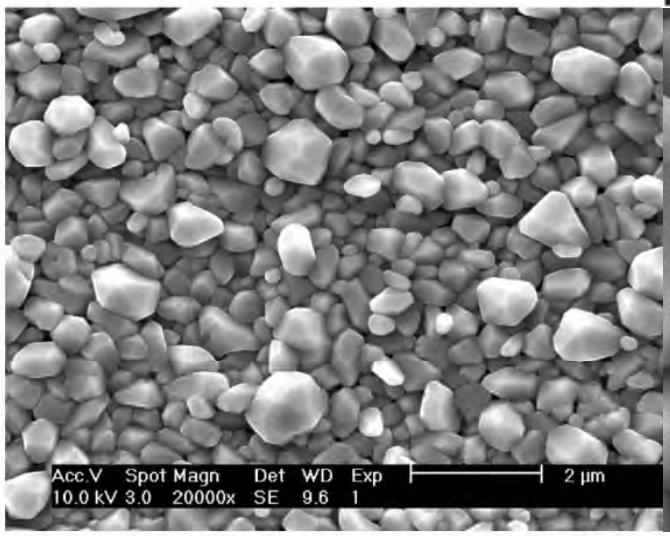
Progress

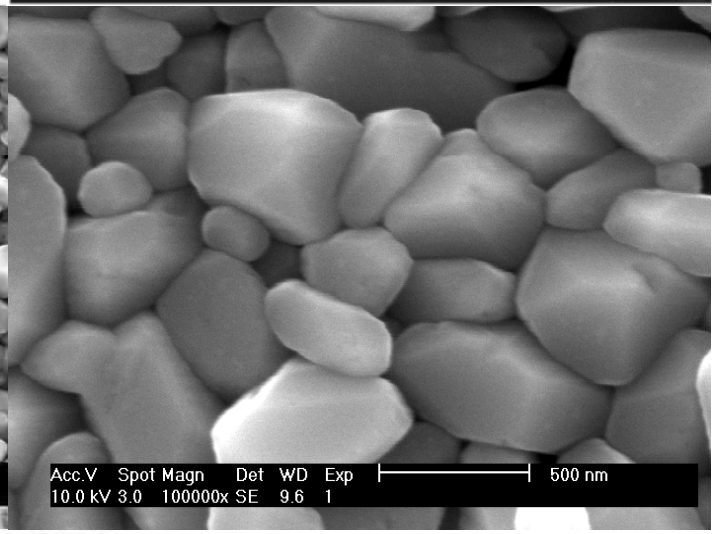
- 7 layer films give nicely connected grains on glass (but rough surface)
- >8 layers?
- “7 + 2” process?



on glass:

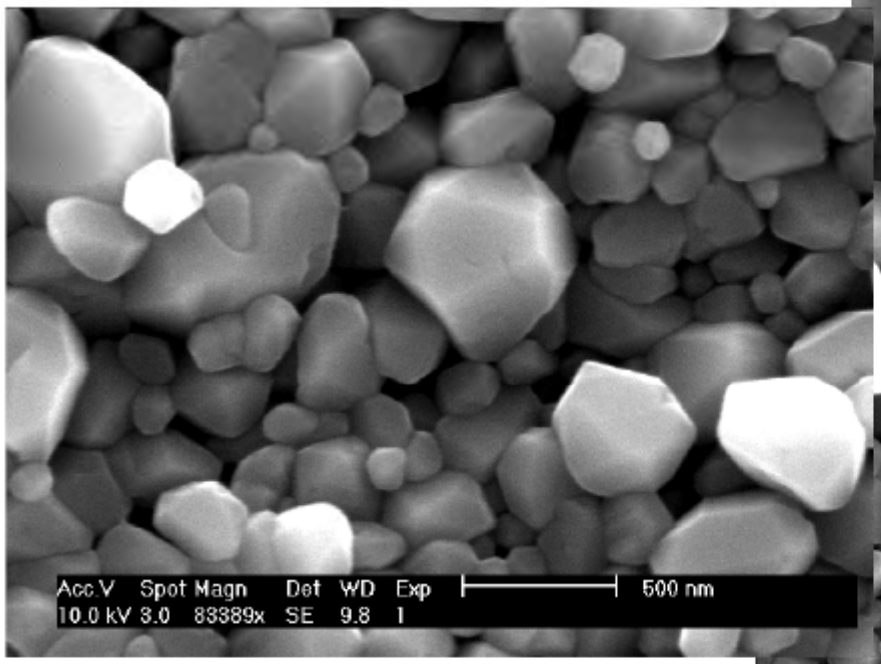


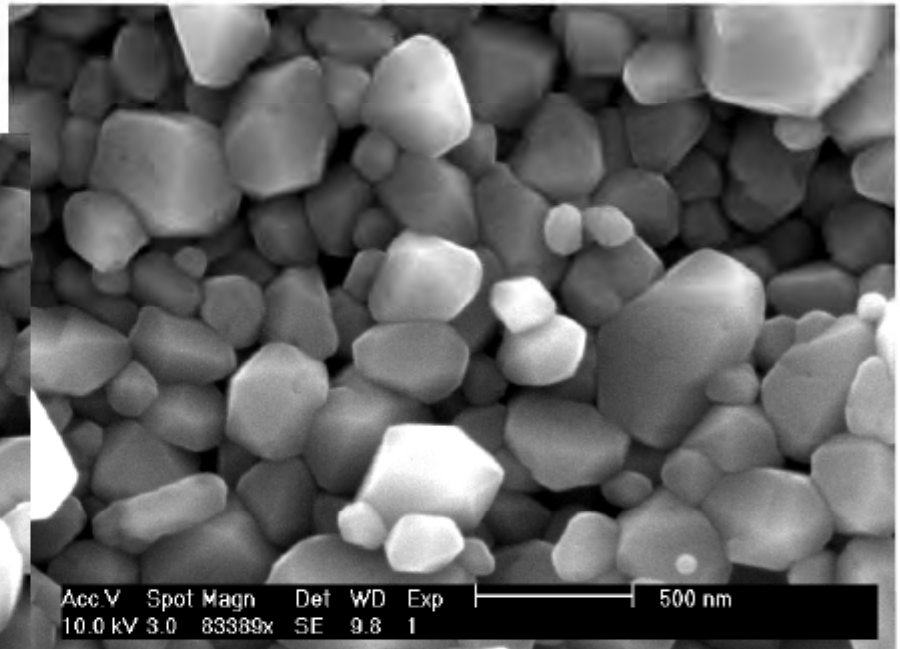


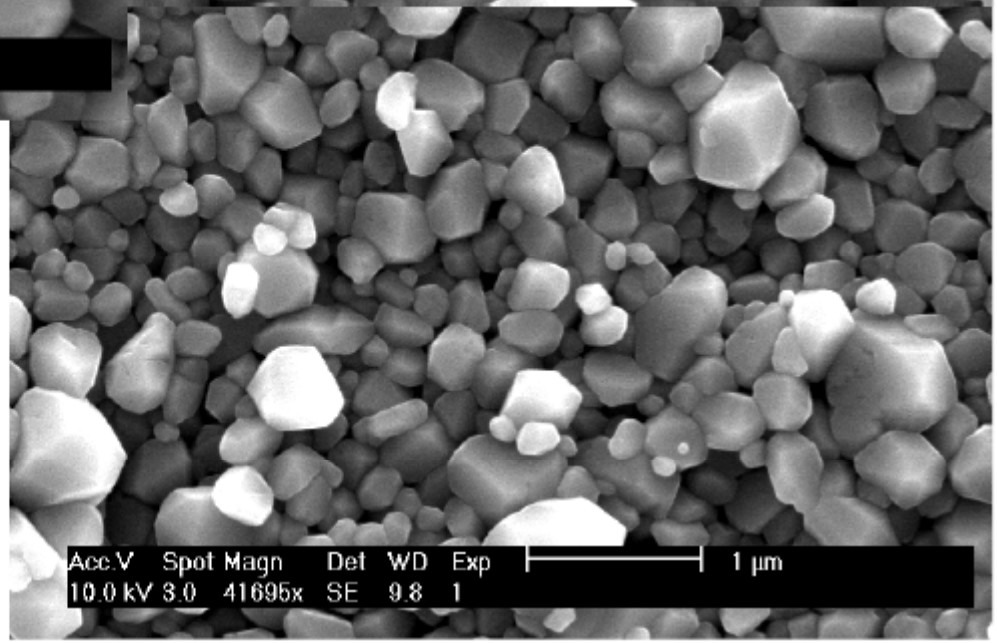


Iron route on glass

SEM: 550C, 6hrs, 25mg S, 7 layers,
#2 (3rd remake attempt)







sodium incorporation almost a certainty (SIMS)

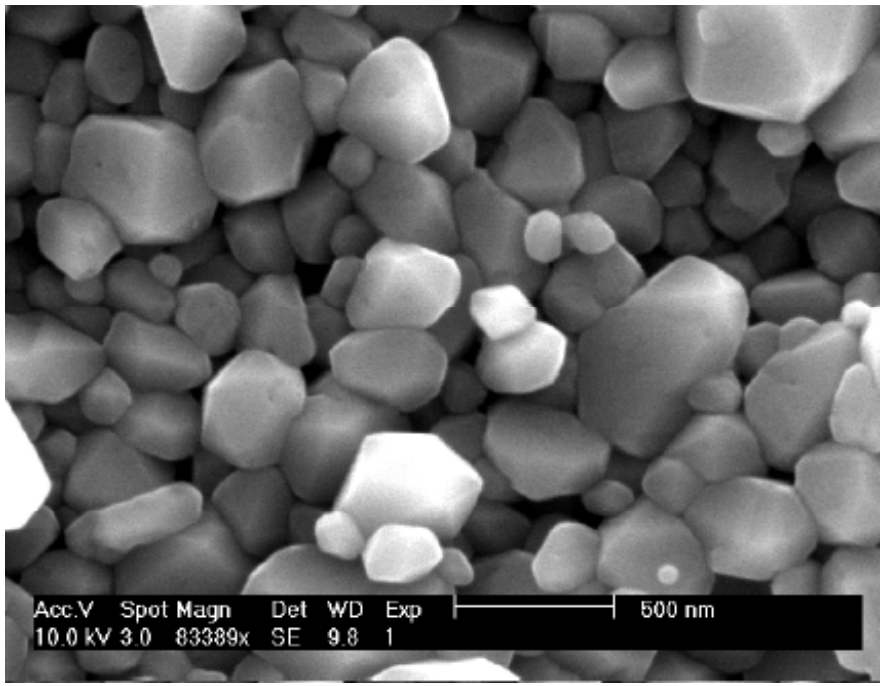
role of sodium in microstructure?

glass vs. quartz

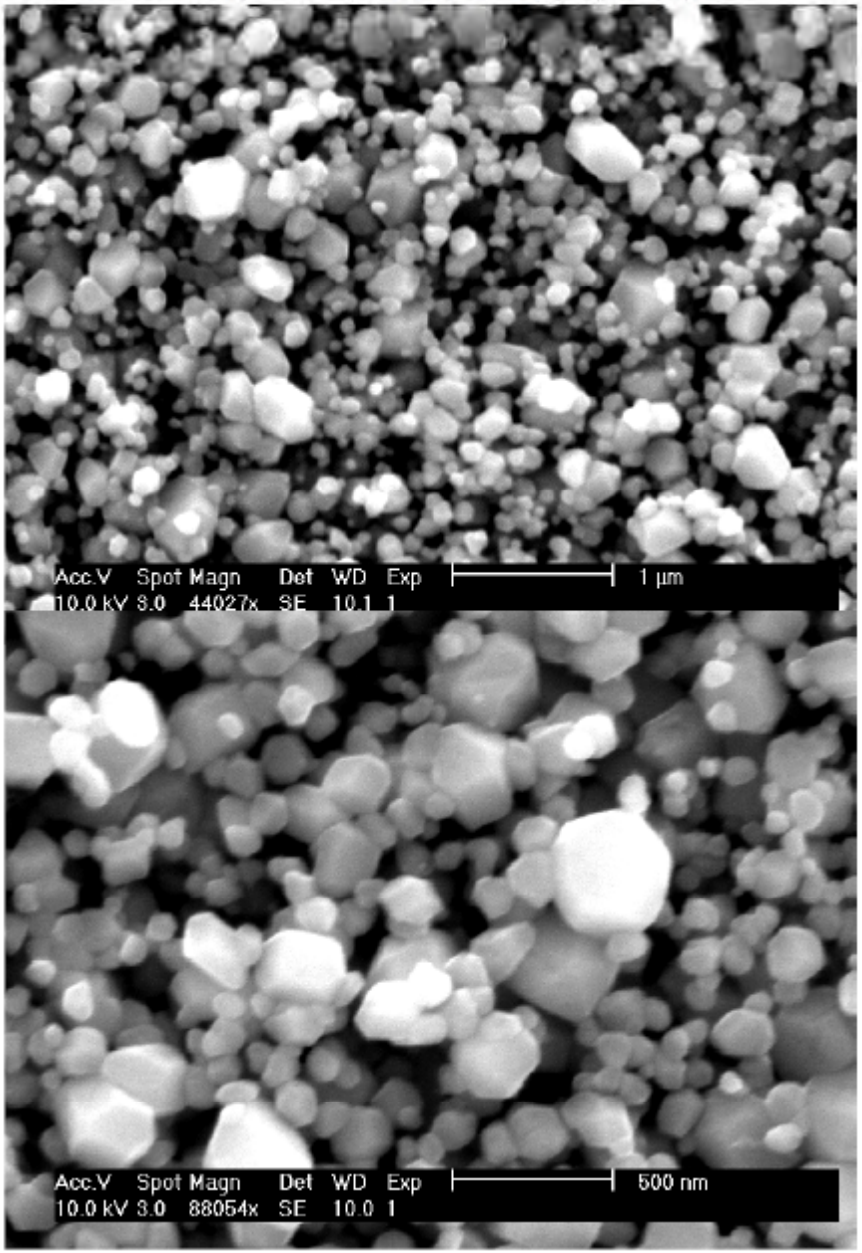
role of sodium in microstructure?

glass:

SEM: 550C, 6hrs, 25mg S, 7 layers, #2 (3rd remake attempt)

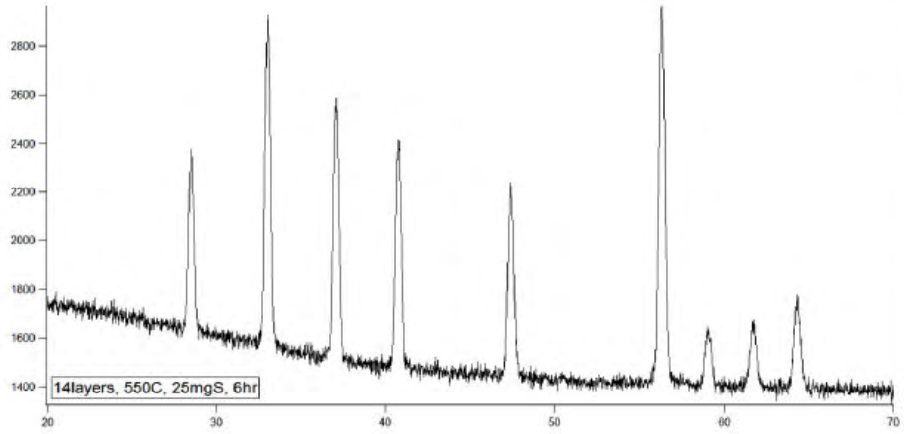


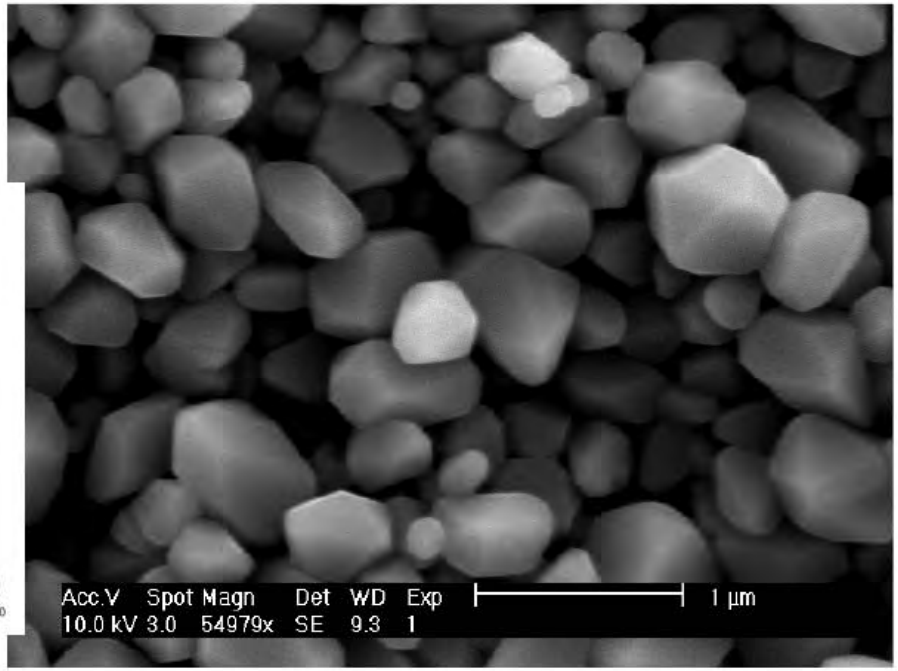
SEM: Quartz, 550C, 6hrs, 25mg S, 7 layers

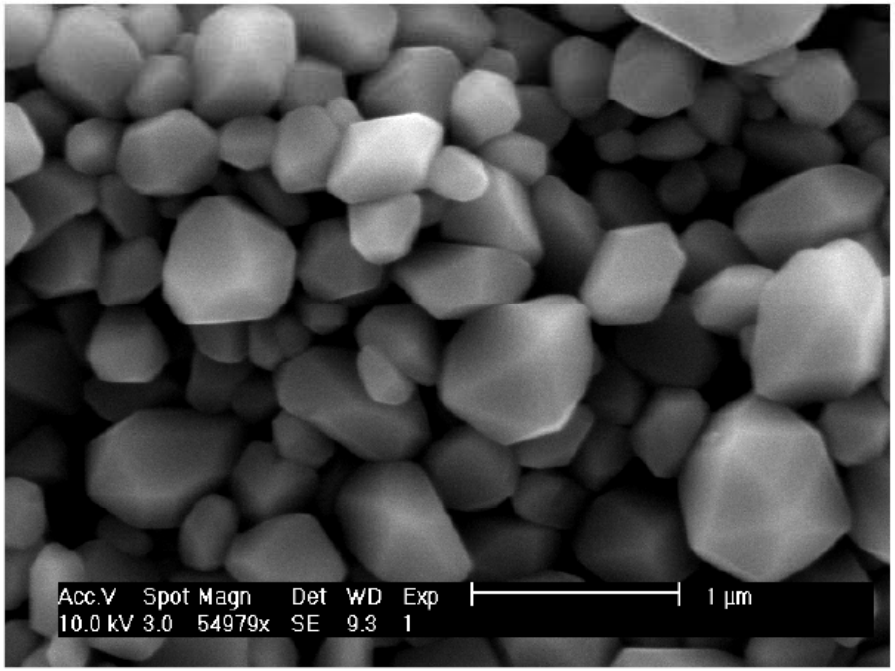


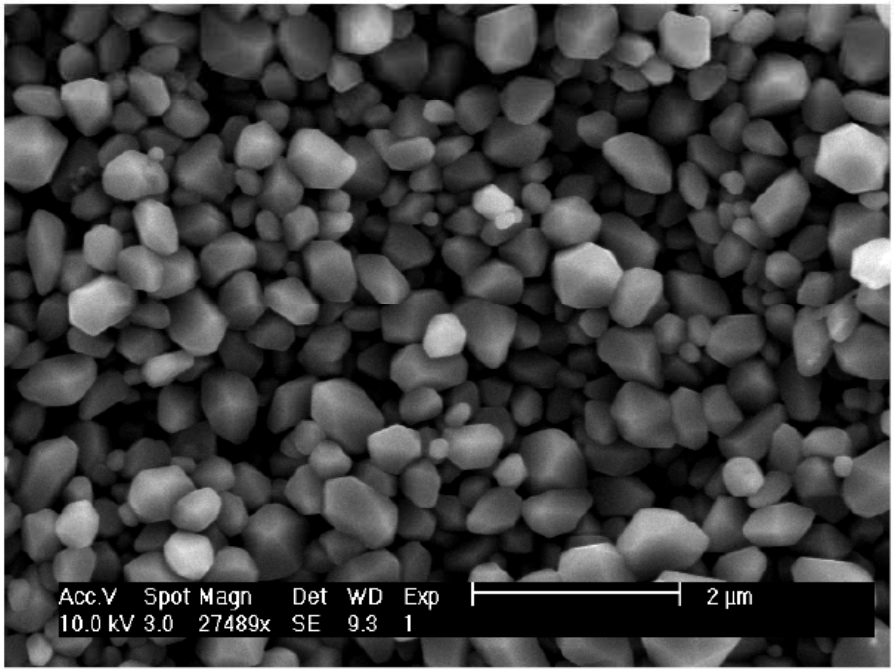
14 layers, 550C, 6hr, 25mg S

probably ~2 um thick



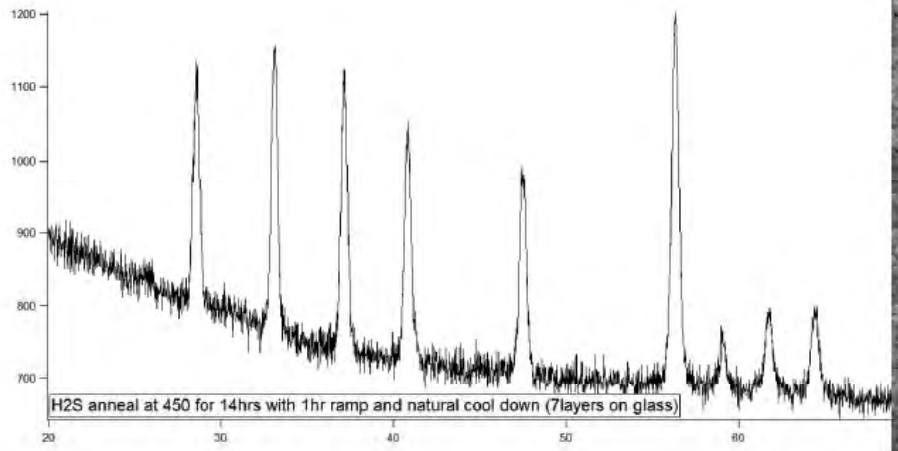


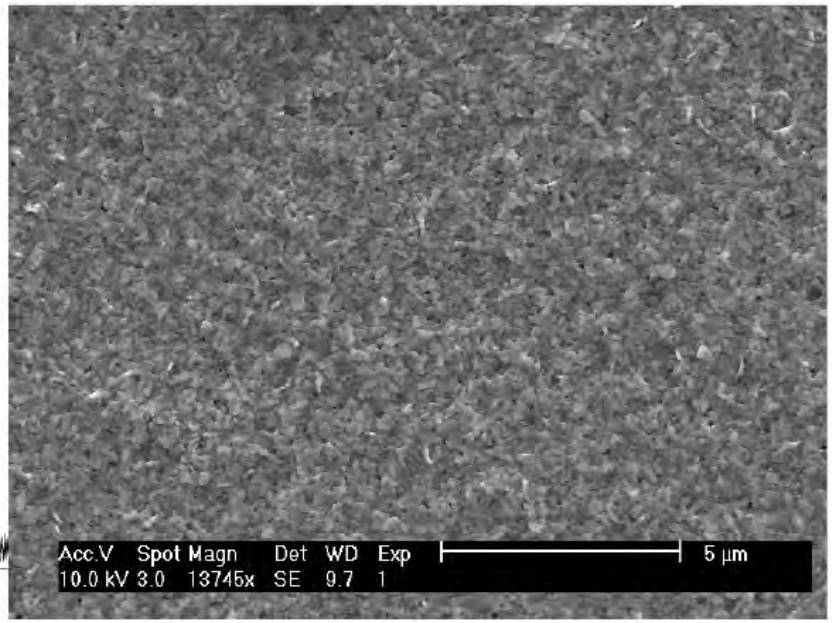


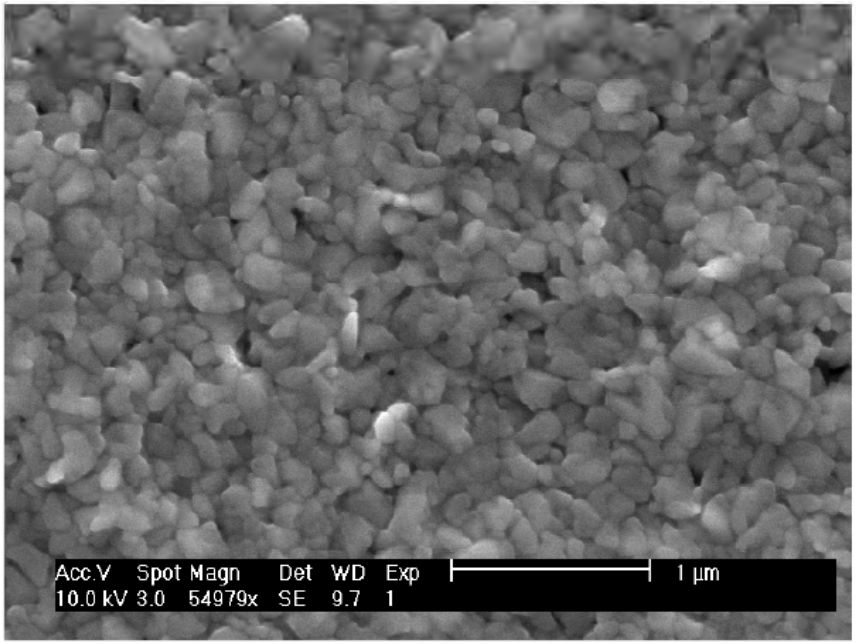


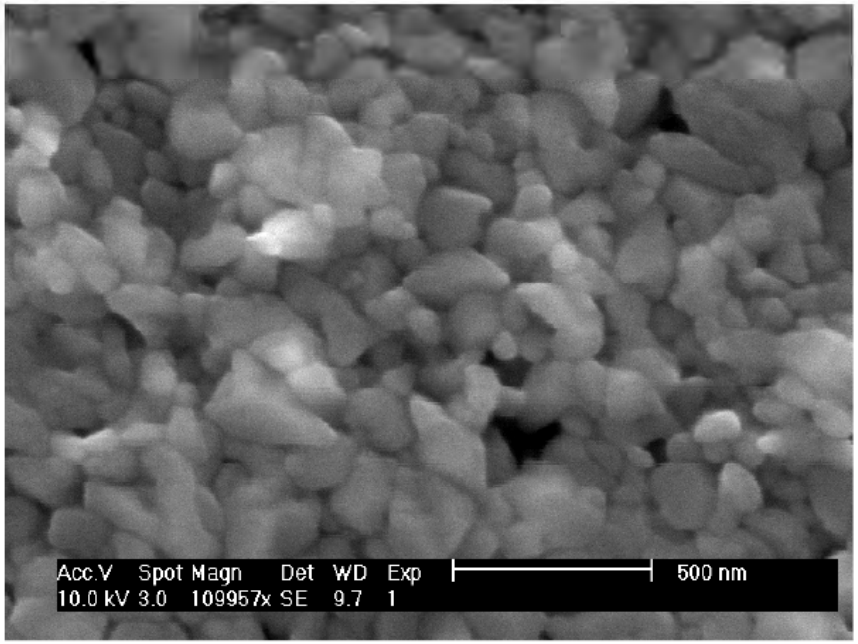
First H_2S sintering results

H_2S Anneal (450C, 14hr, 1hr ramp, natural cool)









Conclusions

- CVD gives nice pyrite films (annealing needed on non-glass substrates). Slow growth rate. Films now being used for XPS. Mobilities appear too small for Hall measurements.

- We have stable pyrite nanocrystal inks and pyrite films from same. Sintered films have large grain size but usually disconnected grains and rough surfaces. Reproducibility is a nagging problem.

- Fe-acac molecular route gives moderately connected, medium grain films with rough surfaces. Multiple spin/sinter steps results in layered films. Carbon deposition during sintering may be hindering grain growth.

- Iron molecular route gives best morphology so far, with most promising stoichiometry. Large (500-1000 nm), well connected grains. Process is reproducible. Substrate effects are apparent. Films are rough. H_2S sintering gives smoother films @ 100-300 nm grain size.