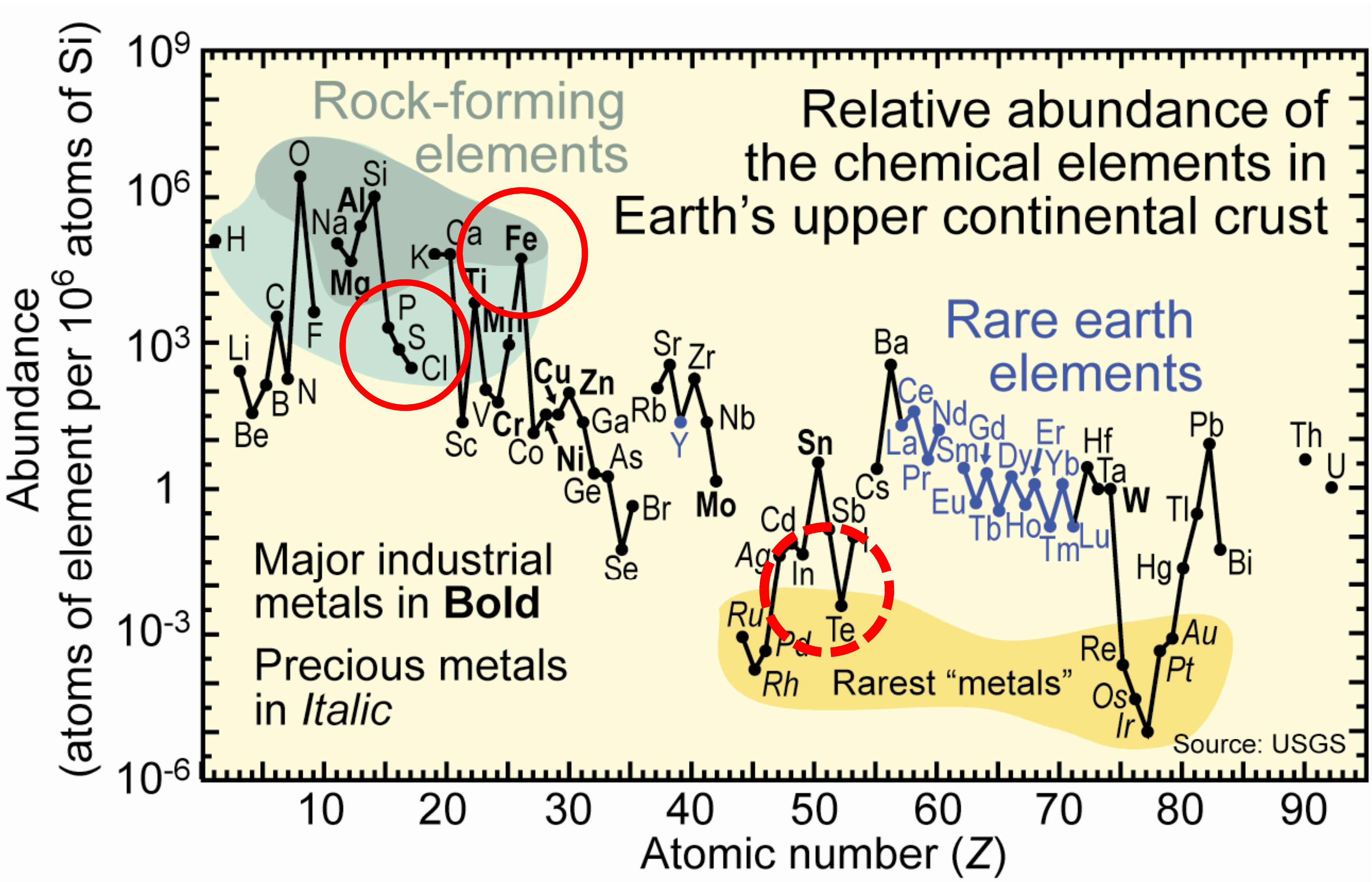
Pyrite FeS_2 Kickoff Meeting

August 3, 2010

Meeting schedule

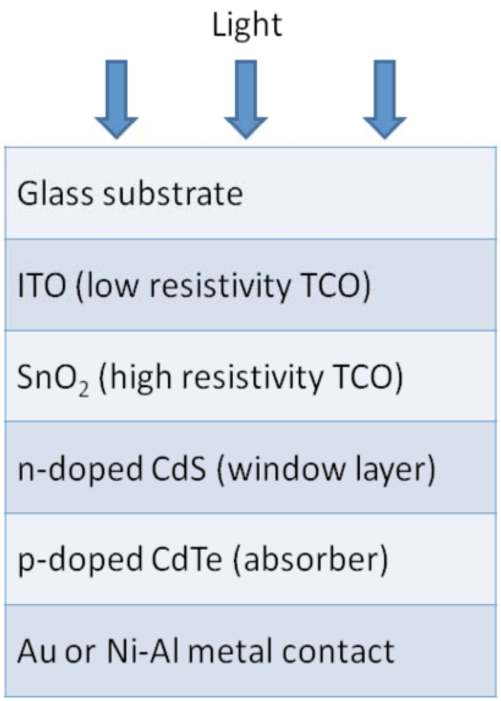
9:00	Intro to pyrite, collaboration	Matt Law
9:20	Phase Field Crystal (PFC) modeling	John Lowengrub
9:40	CVD thin film growth	Nick Berry
9:55	XPS analysis of pyrite films	Ming Cheng
10:10	Colloidal pyrite nanocrystals and films	James Puthussery
10:25	Colloidal & molecular approaches	Sean Seefeld
10:40	New ligands / Molecular approaches	Amanda Weber
10:55-12:00	Discussion and planning	

Earth-abundant materials for photovoltaics (PV)



The dominant thin film technologies (CdTe, $CuIn_xGa_{1-x}Se_2$) are based on rare, toxic elements.

First Solar – CdTe thin film company



Light

Glass substrate

ITO (low resistivity TCO)

SnO_2 (high resistivity TCO)

n-doped CdS (window layer)

p-doped CdTe (absorber)

Au or Ni-Al metal contact

- Largest thin film manufacturer
- 1.25 GW/yr manufacturing capacity in 2010, projected 1.8 GW/yr in 2012
- $0.85/watt module manufacturing cost (3Q 2009), versus crystalline silicon which is closer to $3/watt
- First Solar's average module efficiency is 11% (3Q 2009)
- Best CdTe cell efficiency is 16.5% (NREL)
- Module cost < 50% total installed cost

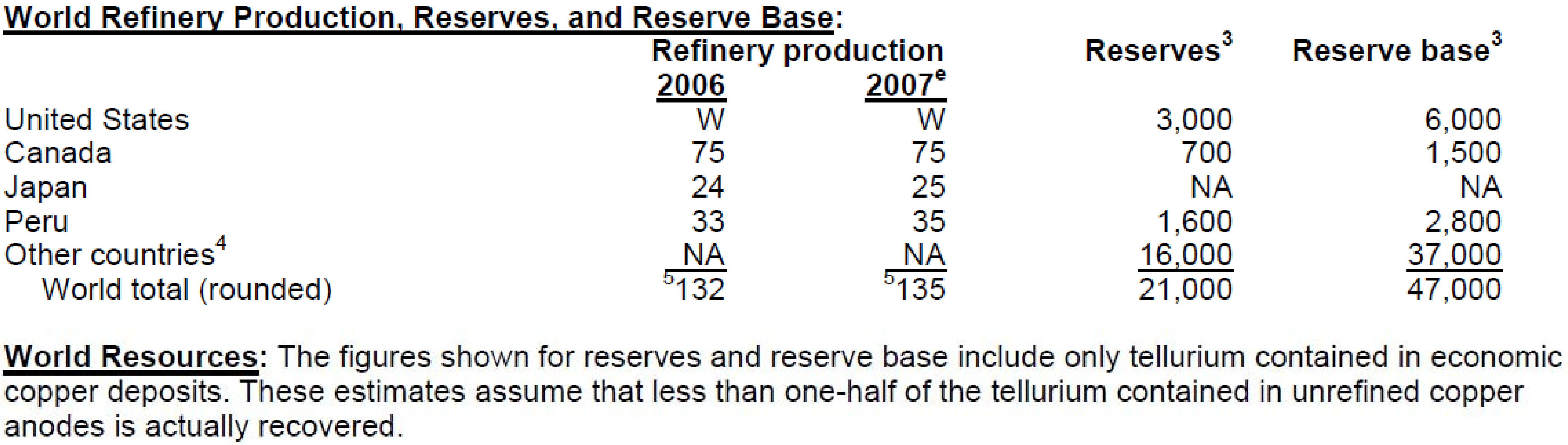
40-MW installation in Waldpolenz, Germany

Thin film array at Dimbach, Germany. 1.3 MW using First Solar Thin Film modules

Scalable to TWs?

Will tellurium limit scalability of CdTe PV?

U.S. Geological Survey, Mineral Commodity Summaries, January 2008



World Refinery Production, Reserves, and Reserve Base:

	Refinery production 2006	Refinery production 2007[e]	Reserves[3]	Reserve base[3]
United States	W	W	3,000	6,000
Canada	75	75	700	1,500
Japan	24	25	NA	NA
Peru	33	35	1,600	2,800
Other countries[4]	NA	NA	16,000	37,000
World total (rounded)	[5]132	[5]135	21,000	47,000

World Resources: The figures shown for reserves and reserve base include only tellurium contained in economic copper deposits. These estimates assume that less than one-half of the tellurium contained in unrefined copper anodes is actually recovered.

- 135 tons Te produced in 2007
- 1 GW CdTe PV uses ~90 tons Te
- 1 TW CdTe would require entire worldwide reserve base

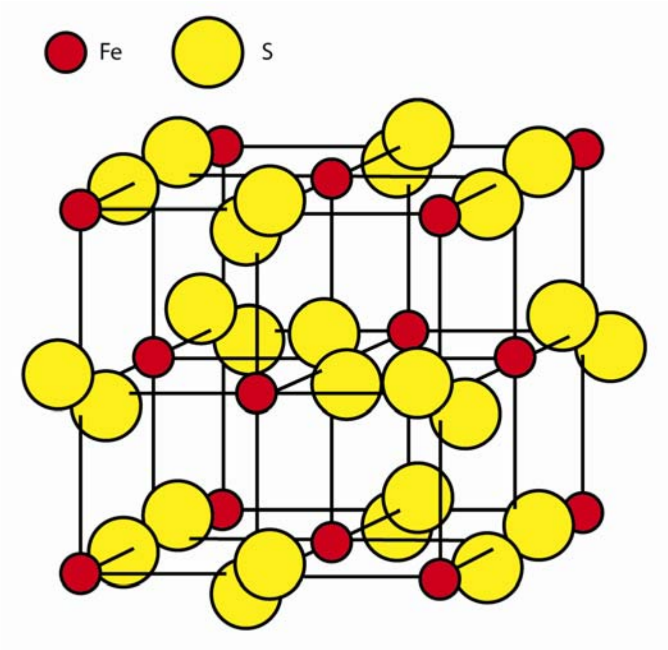
… More Te will have to be found/mined economically

Iron Pyrite (FeS_2)

Fool's gold

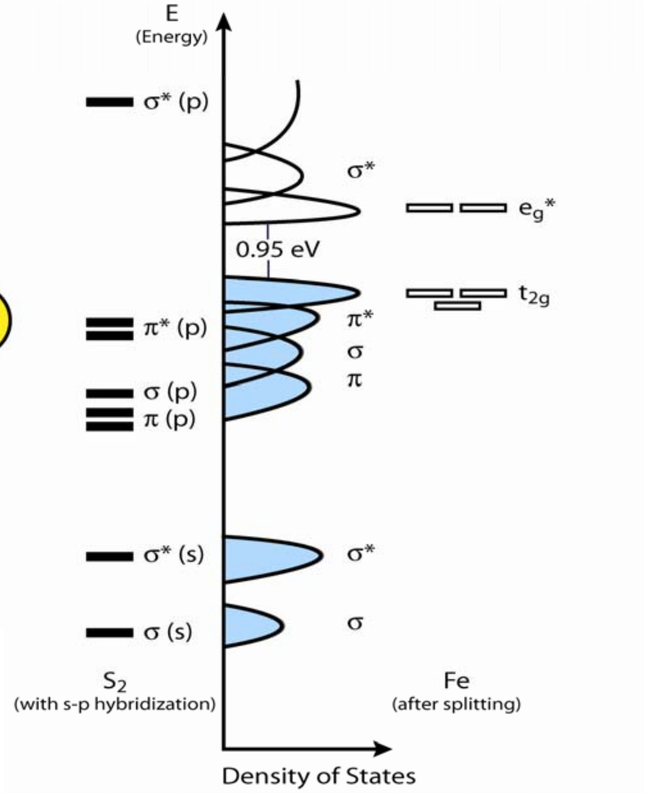
- suitable bandgap (0.95 eV)
- very strong light absorption
- adequate diffusion lengths
- extremely cheap
- infinitely abundant (most abundant sulfide in crust)

Crystal structure



Space group Pa3

Electronic structure



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

Basic properties

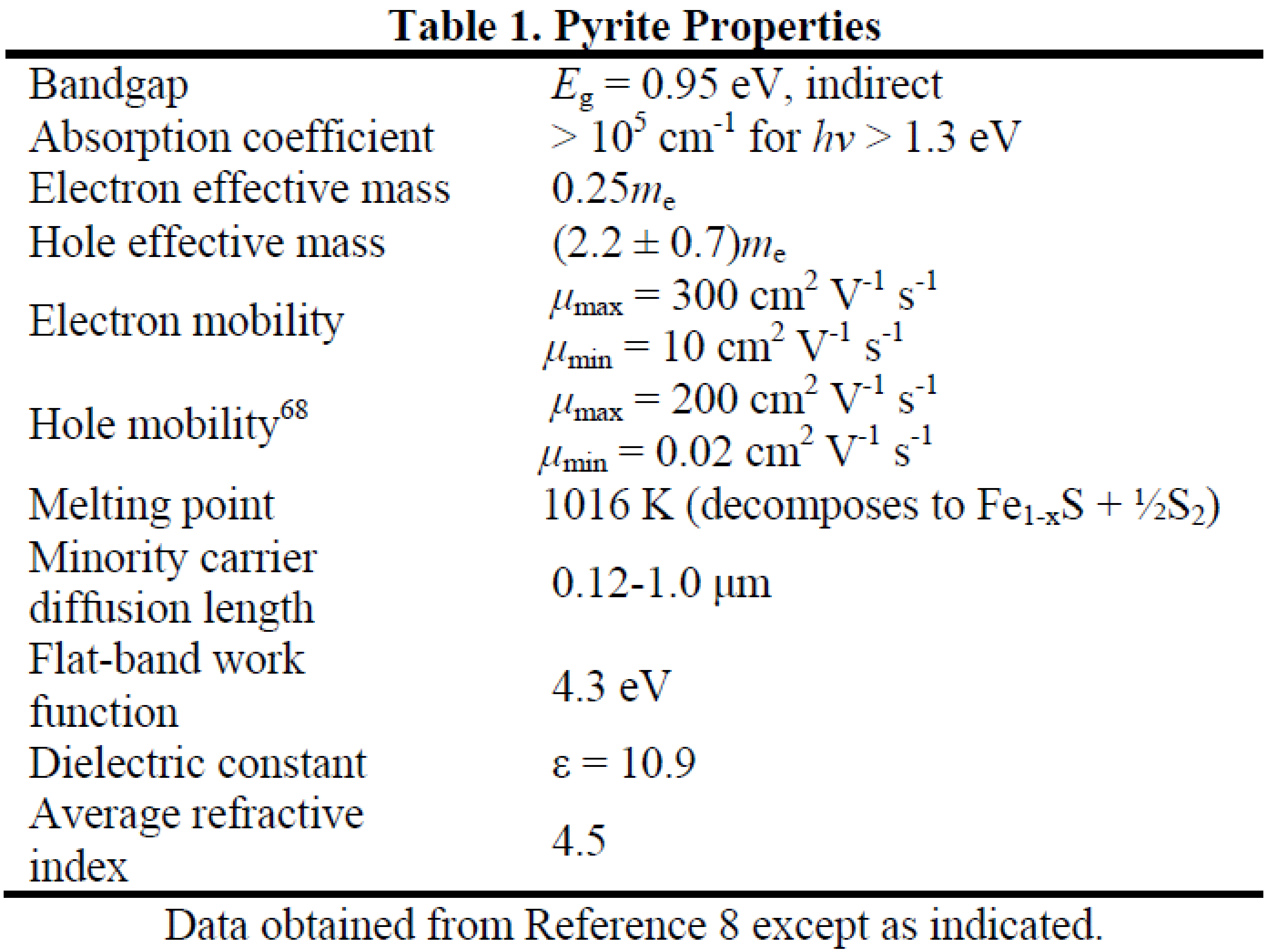


Table 1. Pyrite Properties

Bandgap	$E_g = 0.95$ eV, indirect
Absorption coefficient	$> 10^5$ cm^{-1} for $h\nu > 1.3$ eV
Electron effective mass	$0.25m_e$
Hole effective mass	$(2.2 \pm 0.7)m_e$
Electron mobility	$\mu_{max} = 300$ cm^2 V^{-1} s^{-1} $\mu_{min} = 10$ cm^2 V^{-1} s^{-1}
Hole mobility[68]	$\mu_{max} = 200$ cm^2 V^{-1} s^{-1} $\mu_{min} = 0.02$ cm^2 V^{-1} s^{-1}
Melting point	1016 K (decomposes to $Fe_{1-x}S + \frac{1}{2}S_2$)
Minority carrier diffusion length	0.12-1.0 μm
Flat-band work function	4.3 eV
Dielectric constant	$\varepsilon = 10.9$
Average refractive index	4.5

Data obtained from Reference 8 except as indicated.

Optical absorptivity

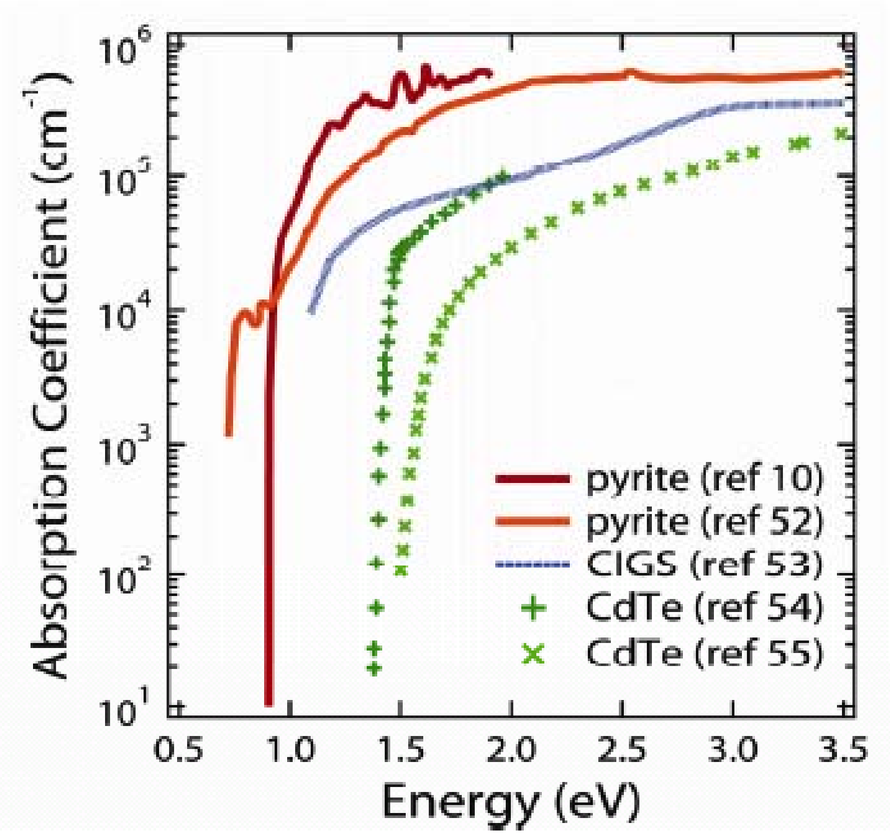


Figure 2.1. Optical absorption coefficients of pyrite, CIGS, and CdTe

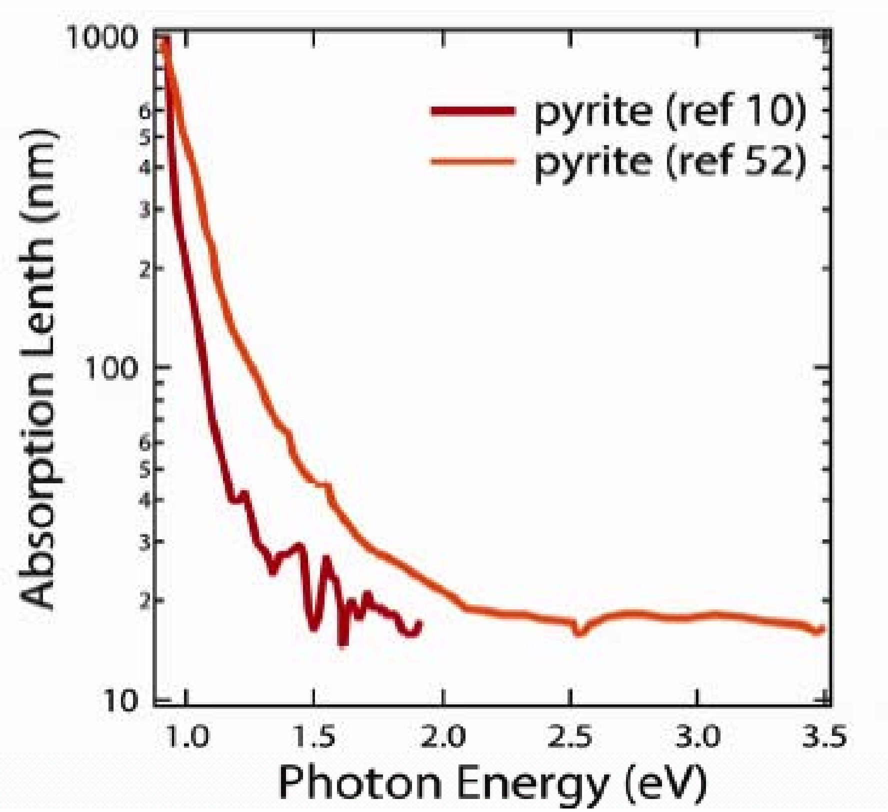


Figure 2.6. Optical absorption length of pyrite films.

Previous work

Helmut Tributsch (Hahn-Meitner Institüt) pioneered pyrite for PV starting in 1983

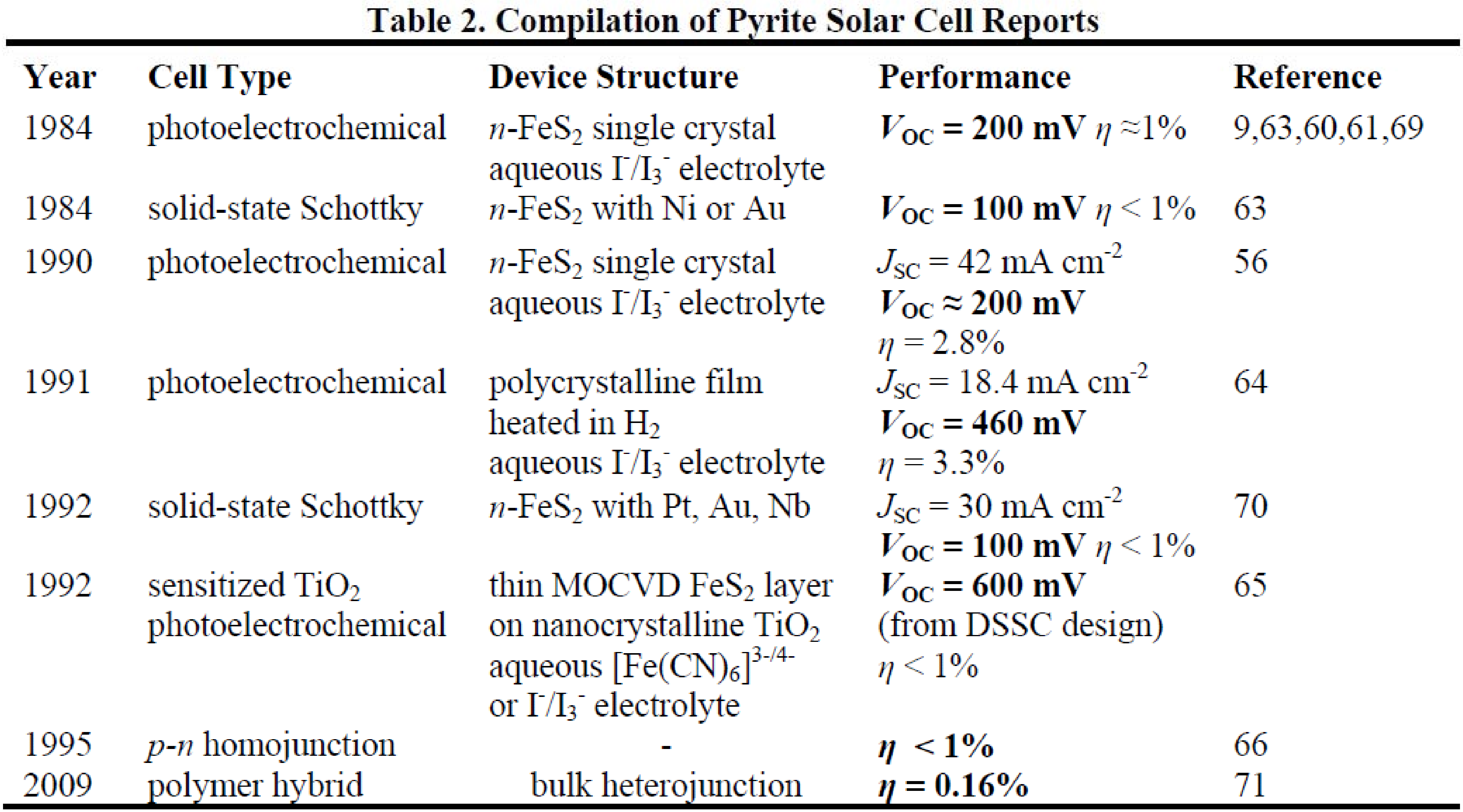


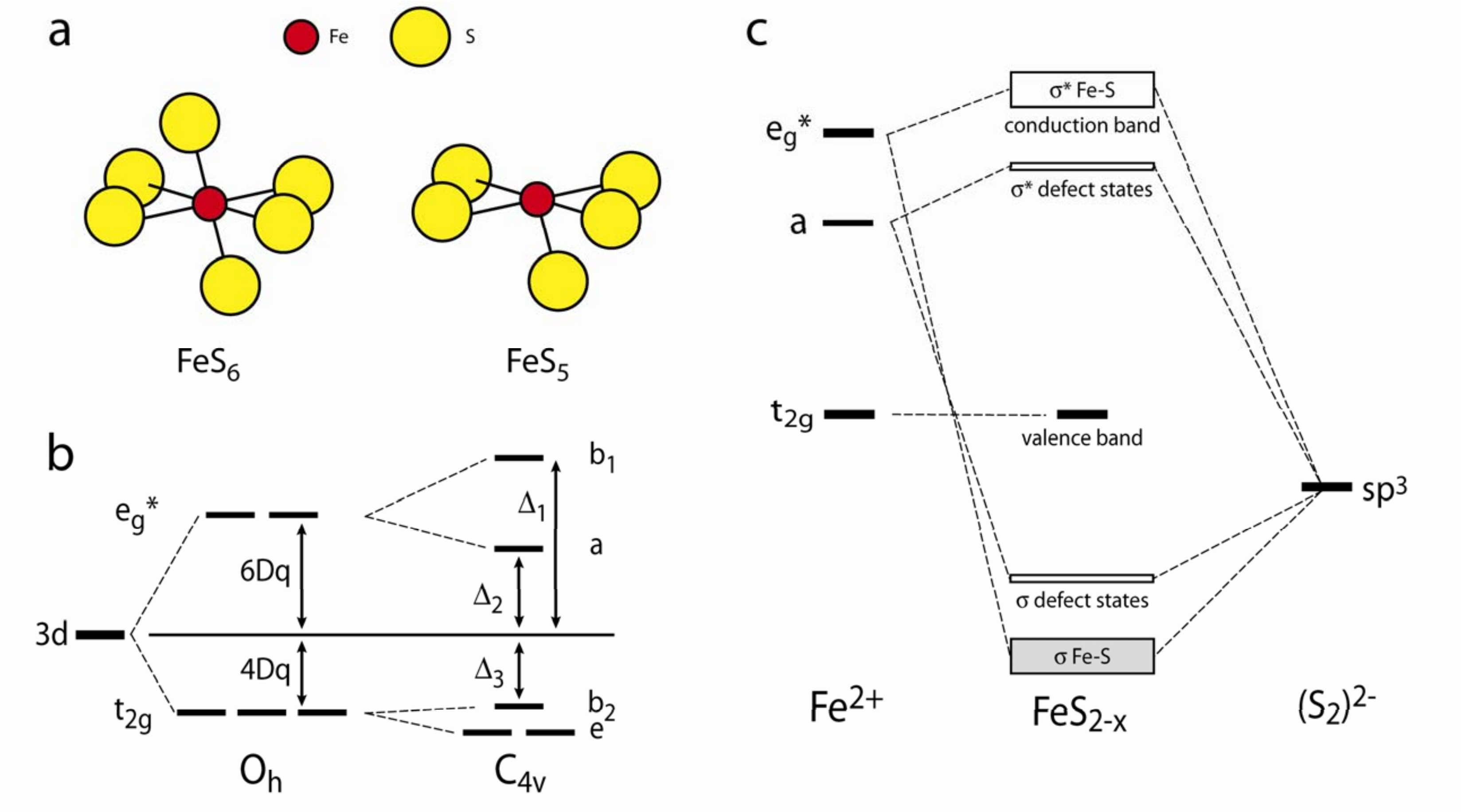
Table 2. Compilation of Pyrite Solar Cell Reports

Year	Cell Type	Device Structure	Performance	Reference
1984	photoelectrochemical	*n*-FeS_2 single crystal aqueous I^-/I_3^- electrolyte	$\mathbf{V_{OC} = 200\ mV}$ $\eta \approx 1\%$	9,63,60,61,69
1984	solid-state Schottky	*n*-FeS_2 with Ni or Au	$\mathbf{V_{OC} = 100\ mV}$ $\eta < 1\%$	63
1990	photoelectrochemical	*n*-FeS_2 single crystal aqueous I^-/I_3^- electrolyte	$J_{SC} = 42\ mA\ cm^{-2}$ $\mathbf{V_{OC} \approx 200\ mV}$ $\eta = 2.8\%$	56
1991	photoelectrochemical	polycrystalline film heated in H_2 aqueous I^-/I_3^- electrolyte	$J_{SC} = 18.4\ mA\ cm^{-2}$ $\mathbf{V_{OC} = 460\ mV}$ $\eta = 3.3\%$	64
1992	solid-state Schottky	*n*-FeS_2 with Pt, Au, Nb	$J_{SC} = 30\ mA\ cm^{-2}$ $\mathbf{V_{OC} = 100\ mV}$ $\eta < 1\%$	70
1992	sensitized TiO_2 photoelectrochemical	thin MOCVD FeS_2 layer on nanocrystalline TiO_2 aqueous $[Fe(CN)_6]^{3-/4-}$ or I^-/I_3^- electrolyte	$\mathbf{V_{OC} = 600\ mV}$ (from DSSC design) $\eta < 1\%$	65
1995	*p*-*n* homojunction	-	$\boldsymbol{\eta < 1\%}$	66
2009	polymer hybrid	bulk heterojunction	$\boldsymbol{\eta = 0.16\%}$	71

Pyrite suffers from a low voltage

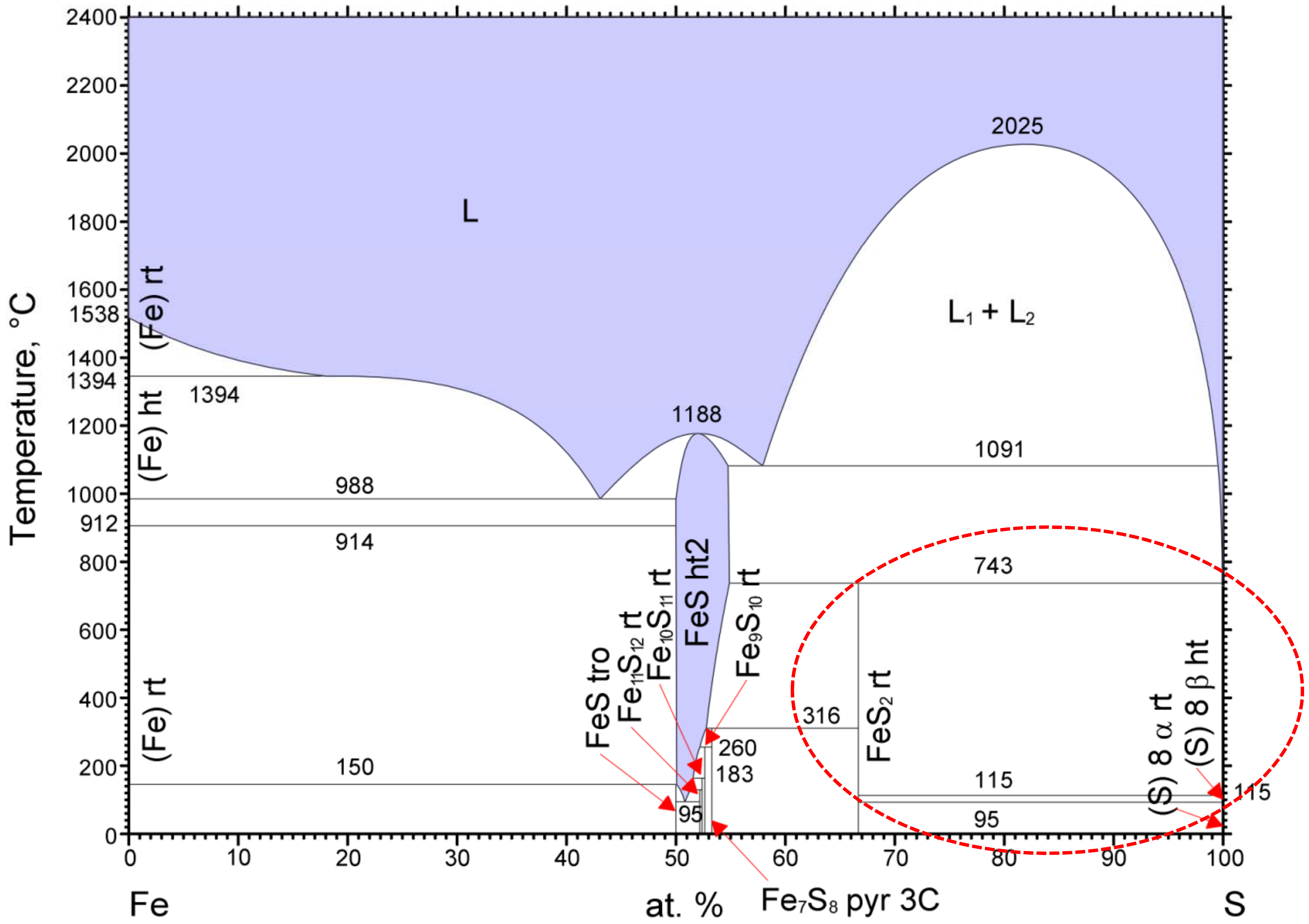
Pyrite tends to be sulfur deficient, and sulfur defects create states in the bandgap, limiting the voltage

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



Passivating bulk/surface defects is the key to boosting cell efficiency

Fe-S phase diagram



Common Fe-S phases

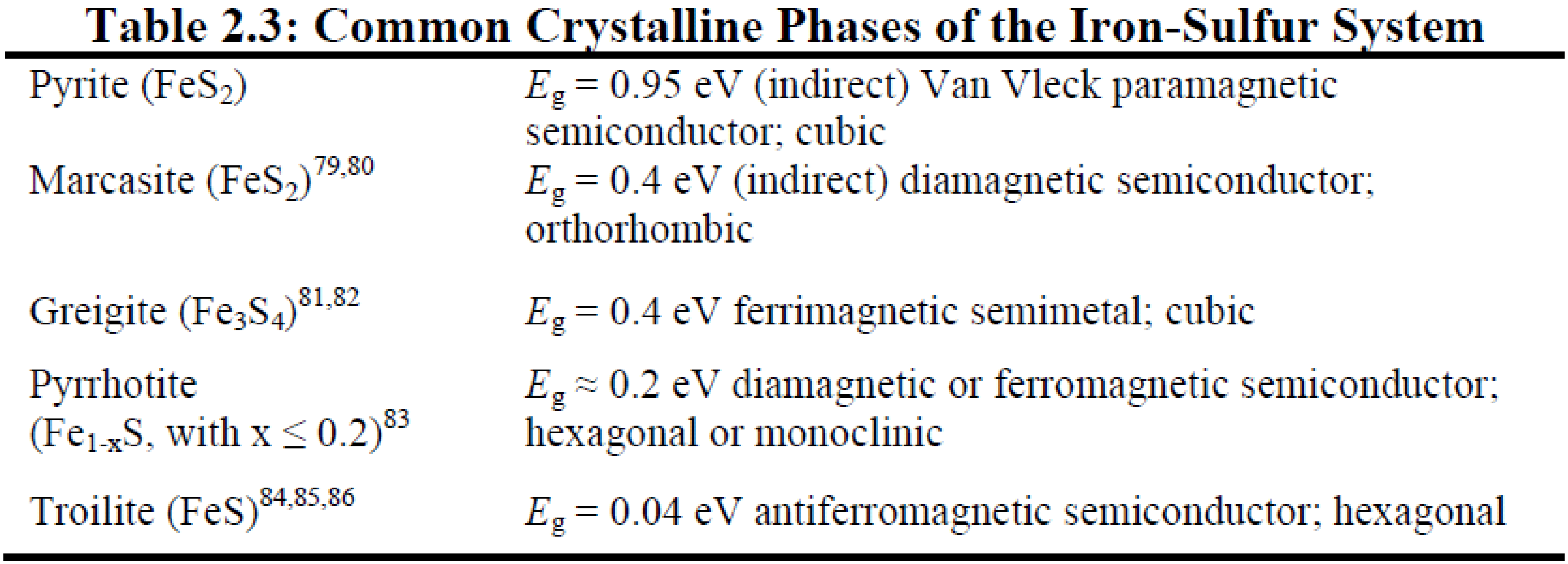


Table 2.3: Common Crystalline Phases of the Iron-Sulfur System

Pyrite (FeS_2)	$E_g = 0.95$ eV (indirect) Van Vleck paramagnetic semiconductor; cubic
Marcasite (FeS_2)[79,80]	$E_g = 0.4$ eV (indirect) diamagnetic semiconductor; orthorhombic
Greigite (Fe_3S_4)[81,82]	$E_g = 0.4$ eV ferrimagnetic semimetal; cubic
Pyrrhotite ($Fe_{1-x}S$, with $x \leq 0.2$)[83]	$E_g \approx 0.2$ eV diamagnetic or ferromagnetic semiconductor; hexagonal or monoclinic
Troilite (FeS)[84,85,86]	$E_g = 0.04$ eV antiferromagnetic semiconductor; hexagonal

Science Summary

- Pyrite is extremely promising as a scalable PV material. It deserves another look, using modern techniques.

- The main limitation on the efficiency of pyrite cells is their low open-circuit voltage.

- The low voltage is probably caused by iron-derived gap states.

- The most promising way to improve the pyrite photovoltage is to passivate under-coordinated iron ions, especially at the crystal surface.

Funding: NSF's SOLAR Program

Synopsis

"The purpose of the CHE-DMR-DMS Solar Energy Initiative is to support interdisciplinary efforts by groups of researchers to address the scientific challenges of highly efficient harvesting, conversion, and storage of solar energy. Groups must include three or more co-Principal Investigators of whom one must be a researcher in chemistry, a second in materials, and a third in mathematical sciences in areas supported by the Divisions of Chemistry, Materials Research, and Mathematical Sciences, respectively. The intent is to encourage new collaborations **in which the mathematical sciences are linked in a synergistic way** with the chemical and materials sciences to develop novel, potentially transformative approaches in an area of much activity but largely incremental advances. Successful proposals will offer potentially transformative projects, new concepts, and interdisciplinary education through research involvement based on the integrated expertise and synergy from the three disciplinary communities."

NSF's emphasis is the math effort: use emerging techniques in math to help mat. sci. and chemistry solve solar problems

SOLAR 2010

- 3rd year of the SOLAR program
- 109 pre-proposals; 30 full proposals; 9 funded
- Our proposal was ranked #1
- We benefitted by <u>not</u> being an organic bulk heterojunction proposal

Collaboration overview

- Objective: Combine PFC and DFT modeling with pyrite growth and surface characterization to
  1) grow device-quality pyrite thin films by 2 methods
  2) triple the pyrite photovoltage via passivation

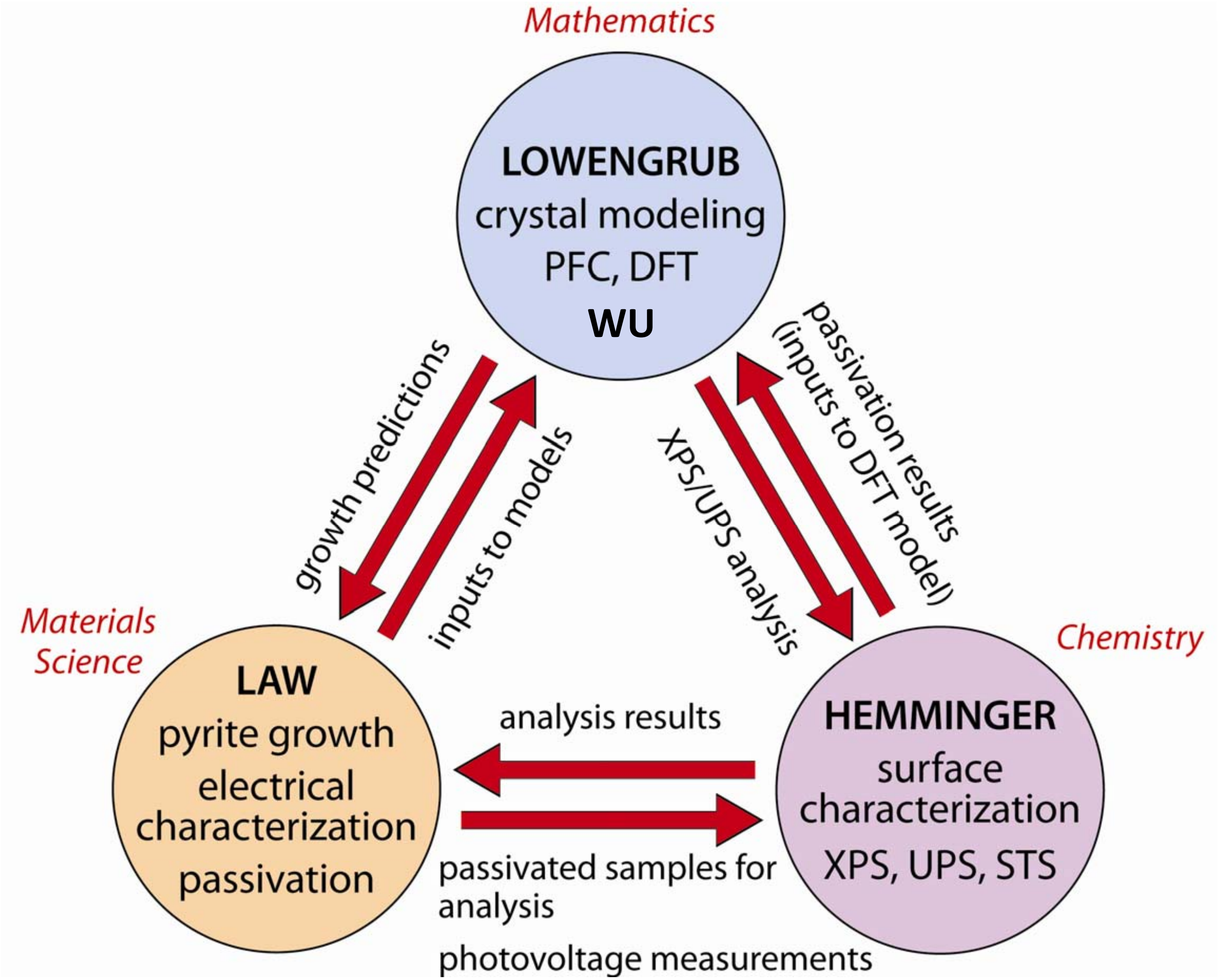
- Law, Hemminger, Lowengrub, and Wu groups.

- 3 years, starting 9/1/10. Project is renewable.

- Funding for 5 students & postdocs.
  - 2 synthesis/characterization (Law)
  - 1 surface characterization (Hemminger)
  - 2 modeling (Lowengrub & Wu)

Collaboration activities

Model • Grow • Characterize



Mathematics

LOWENGRUB
crystal modeling
PFC, DFT
WU

growth predictions

inputs to models

XPS/UPS analysis

passivation results
(inputs to DFT model)

Materials Science

LAW
pyrite growth
electrical characterization
passivation

Chemistry

HEMMINGER
surface characterization
XPS, UPS, STS

analysis results

passivated samples for analysis
photovoltage measurements

Modeling objectives

Angstrom-to-micron capabilities

PFC

Ideally, show how to grow large grain, stoichiometric pyrite thin films.

More realistically, help to:

- control gas-phase pyrite nucleation
- understand crystal growth
- predict crystal phase
- identify conditions for sintering
- understand SS diffusion
- improve adhesion to substrate
- eliminate voids
- minimize sulfur deficiency
- identify conditions for epitaxy

DFT

Ideally, show how to passivate bulk/surface states to boost voltage.

More realistically, help to:

- identify origin of gap states
- calculate binding energies/geometries
- calculate formation energies
- vet promising surface treatments
- interpret/predict XPS results
- interpret/predict STS results
- simulate FTIR data
- discriminate bulk/surface effects
- understand doping

Technical challenges

1. Develop and validate a PFC model for FCC pyrite
2. Develop a DFT model of pyrite (bulk & surface)

With input from the models,

3. Produce high-quality pyrite films from pyrite nanocrystal paint.
4. Make high-quality pyrite films by CVD.
5. Grow epitaxial layers on silicon as model systems.
6. Develop surface passivation treatments that increase the pyrite photovoltage > 500 mV.
7. Establish causation between passivation and enhanced electronic performance. Maximize robustness of passivation.
8. By the end of the project, fabricate prototype pyrite p-n heterojunction solar cells with improved voltage and conversion efficiency.

Surface passivation strategies

- Moderate-temperature annealing in S_2, H_2S, and H_2 atmospheres.
- Coordination of surface iron with strongly-bound organic and inorganic ligands.

Testing with XPS, STS, and photovoltage measurements

Project schedule

Year 1: Construct PFC and DFT models and use to
optimize film microstructure
tune passivation treatments
interpret XPS/UPS/STS data

Year 2: Continuation

Year 3: Be producing high-quality pyrite via both synthetic approaches. Establish the connection between microstructure, gap states, and photovoltage.
By the end, make record-performance devices.

End game

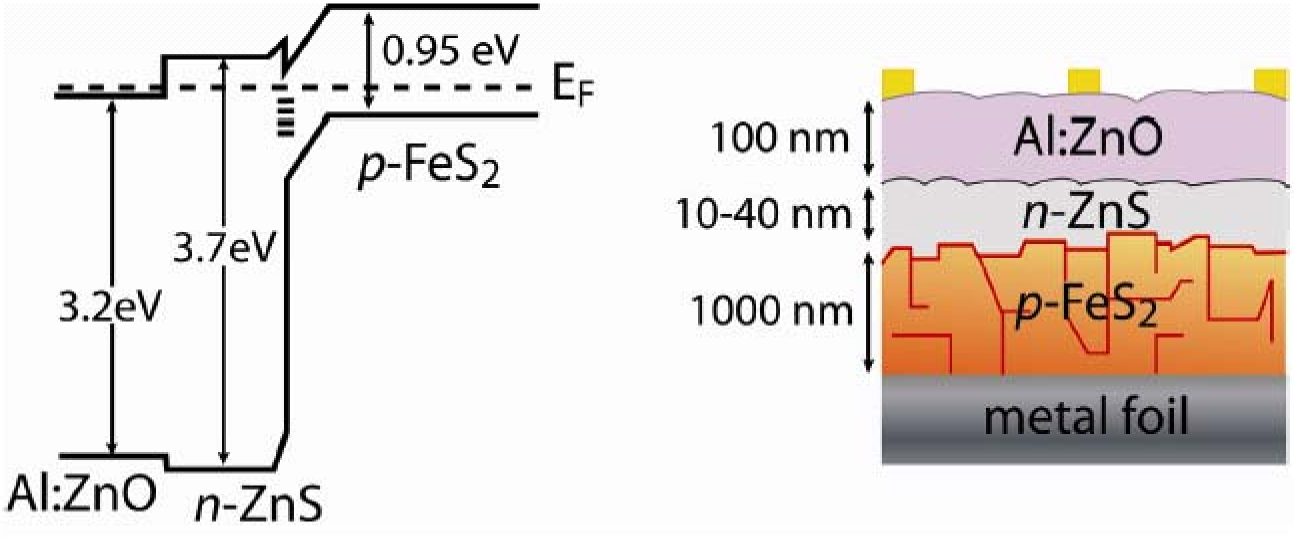
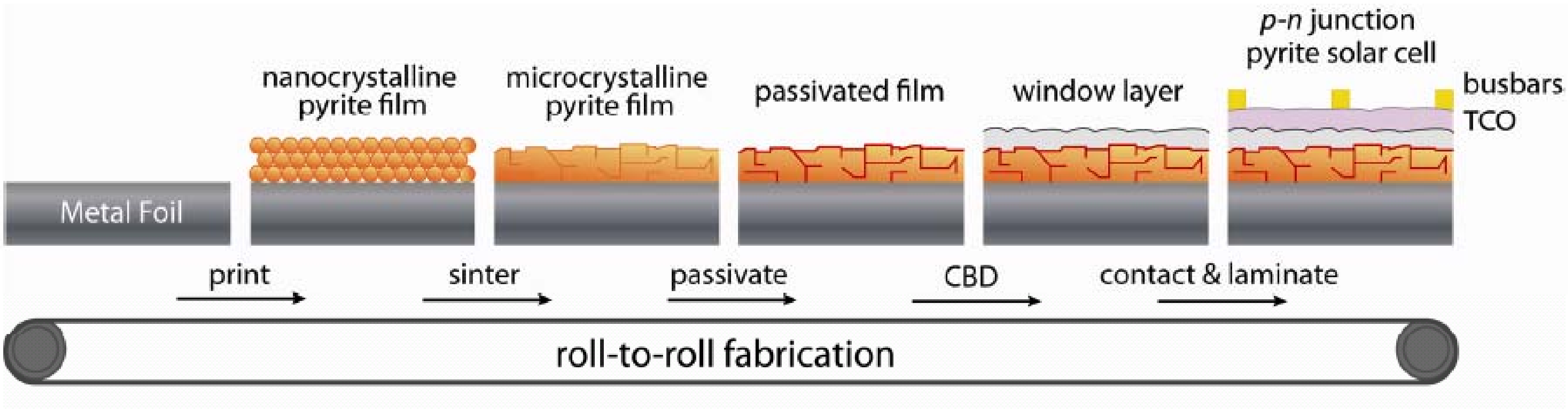


Figure 2.7. (*left*) Band diagram of the heterojunction cell. (*right*) The device structure.



Meeting schedule

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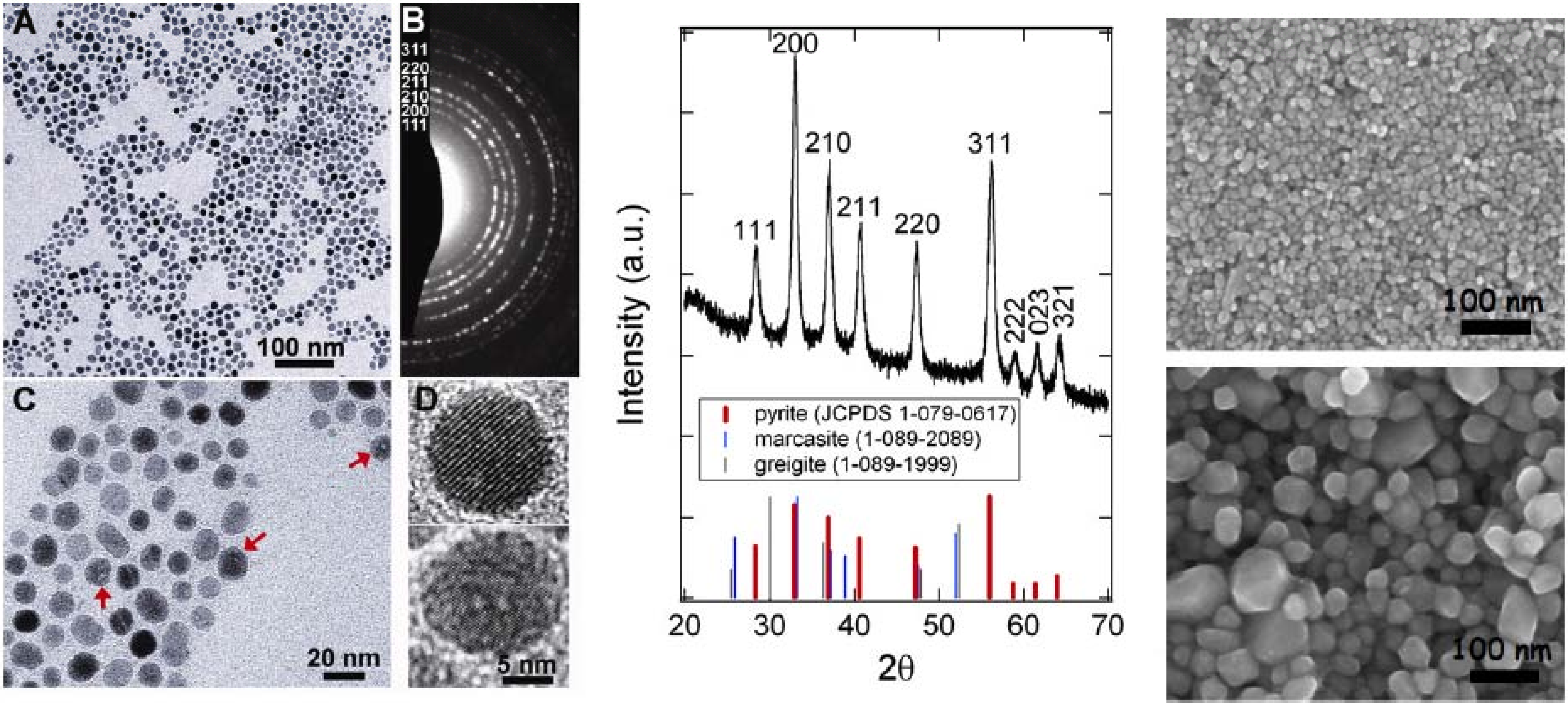


Figure 6. Preliminary data. (*left, middle*) Characterization of colloidal pyrite nanocrystals. (*right*) A pyrite nanocrystal film before (*top*) and after (*bottom*) sintering at 500°C in S_2 vapor.

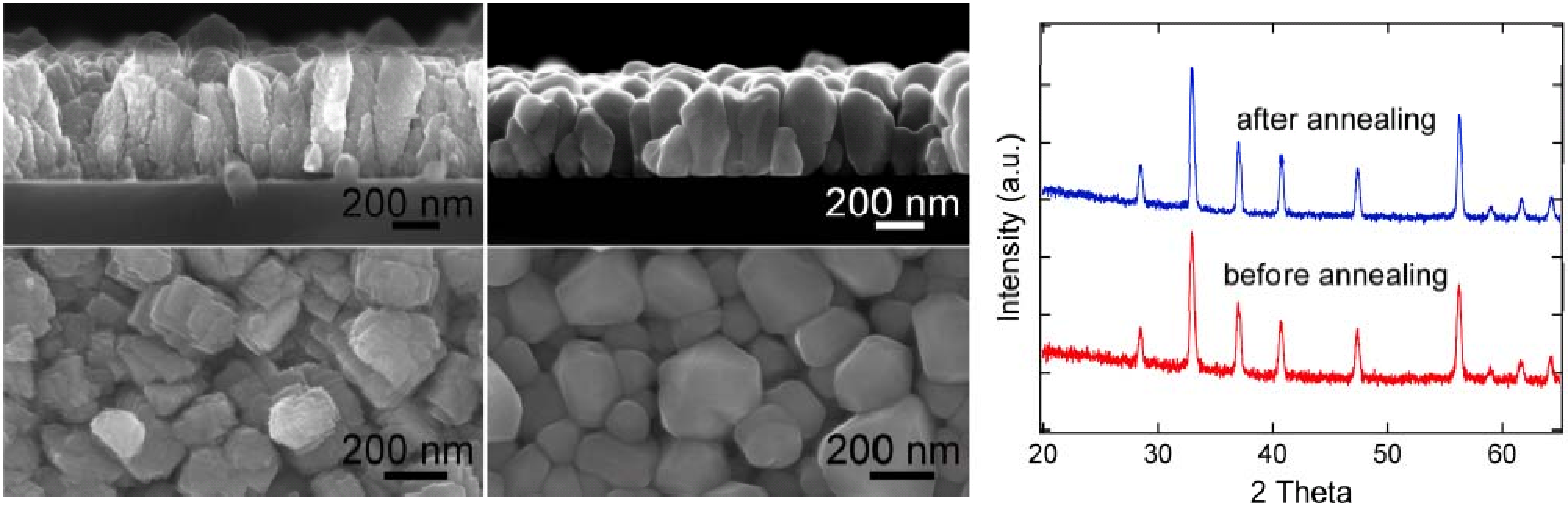
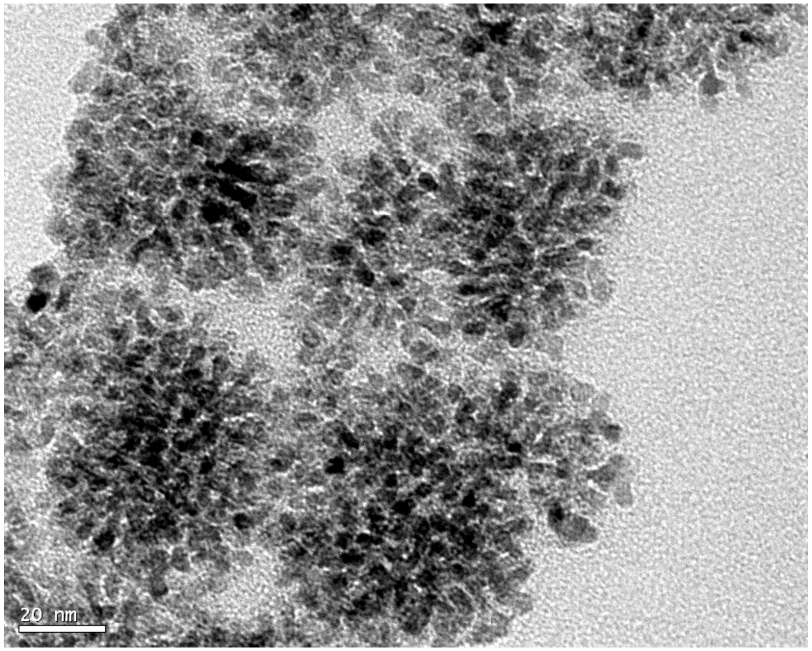


Figure 7. Preliminary data. SEM images of a pyrite thin film grown by CVD on glass before (*left*) and after (*middle*) sintering at 500°C in S_2 vapor. XRDs (*right*) show the film remains pure pyrite.

Synthesizing pyrite NCs is a challenge

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

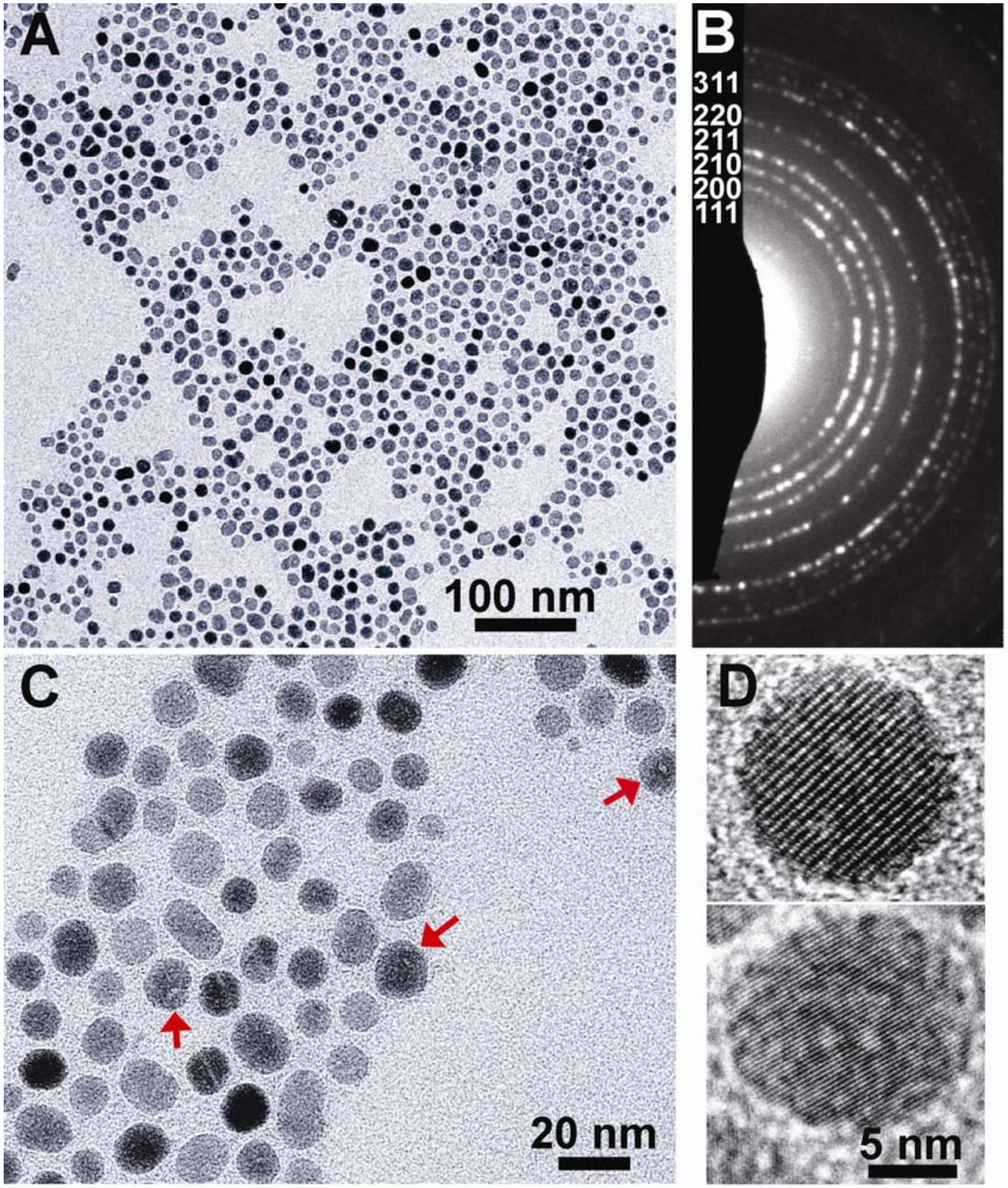
Early results: aggregates

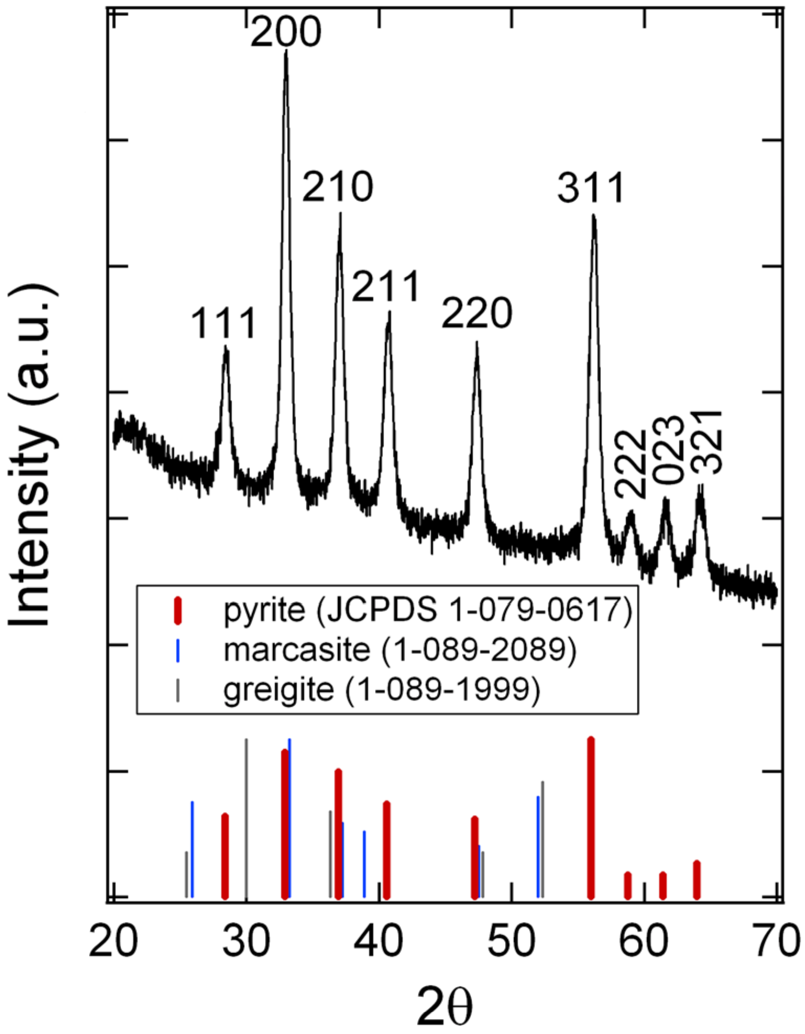


Iron sulfide phases

Pyrite (FeS_2)	cubic, E_g = 0.95 eV (indirect) Van Vleck paramagnetic semiconductor
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

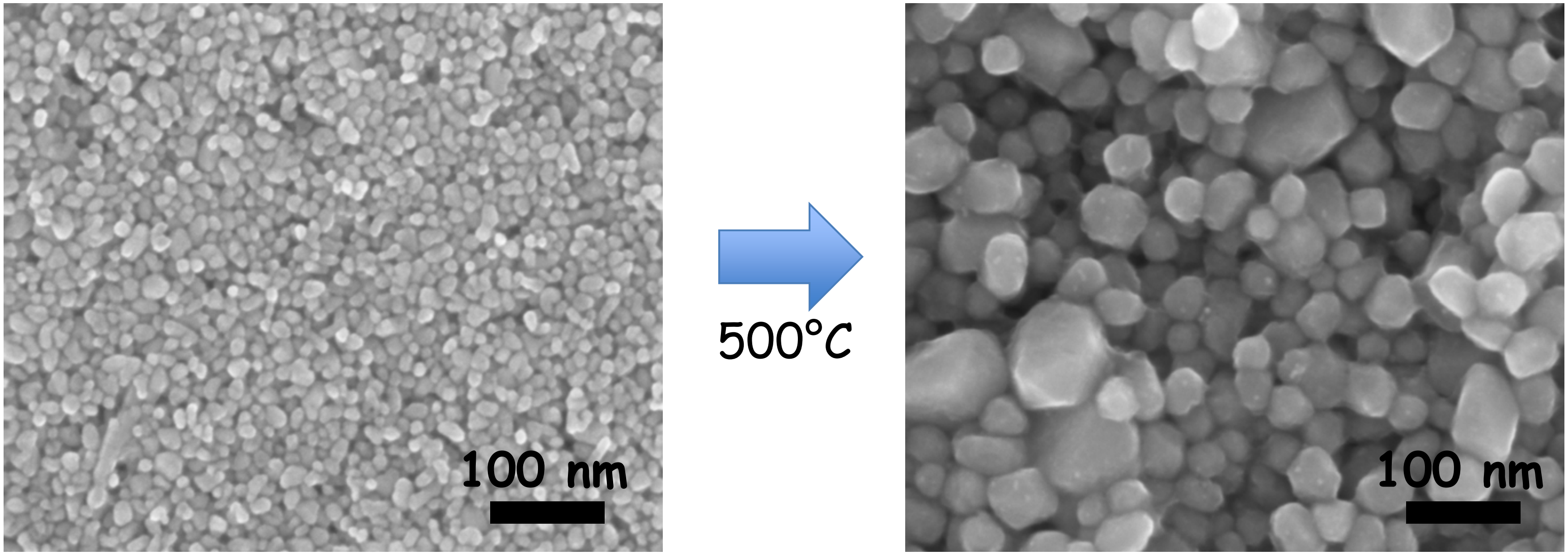
Pyrite nanocrystal inks

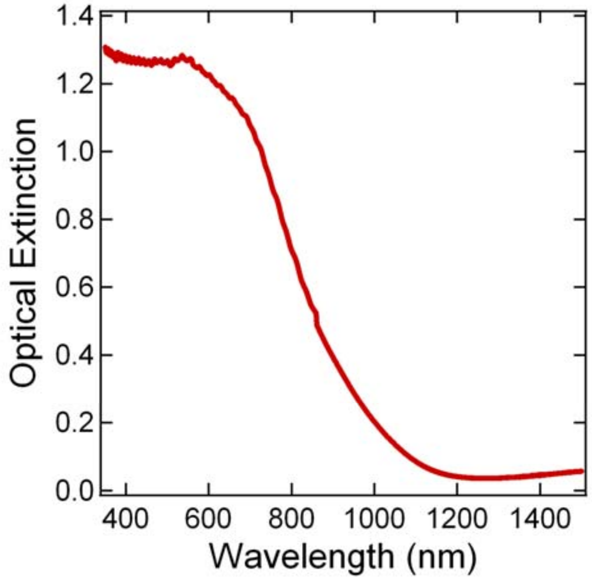




Polycrystalline pyrite thin films

Sintering the NC films in S_2 gas gives polycrystalline pyrite





- film optimization
- characterization
- surface passivation
- devices