

Why does pyrite have a low photovoltage?

August 25, 2011



Hypothesis I: metallic phase impurities

Pyrite always contains metallic FeS-type phase impurities, which somehow reduce the photovoltage

Evidence for it:

- large bulk defect formation energies (DFT) suggest pyrite is $\text{FeS}_{2.00}$
- some calculations show sulfur-deficient phases form spontaneously
- TEM of pyrite films with S:Fe = 1.6 show amorphous regions

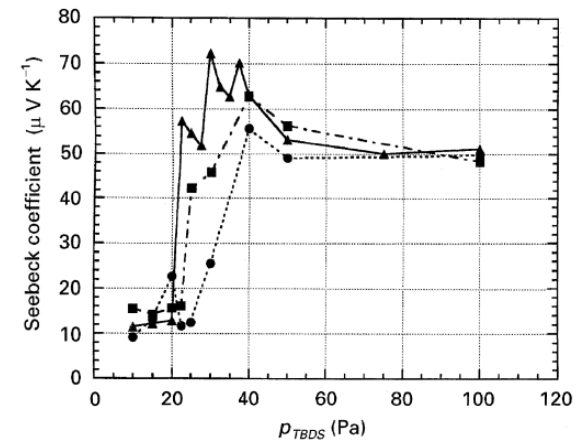
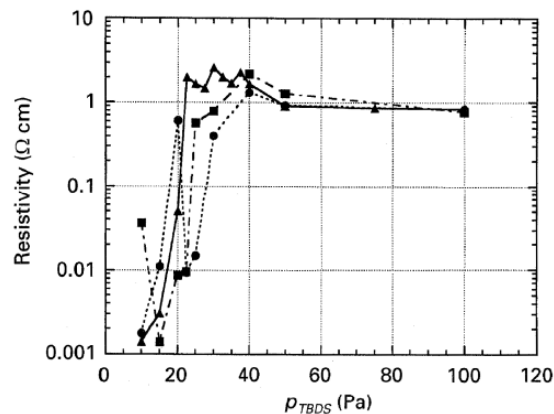
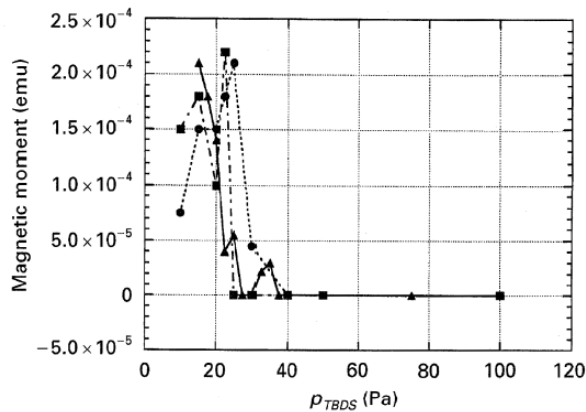
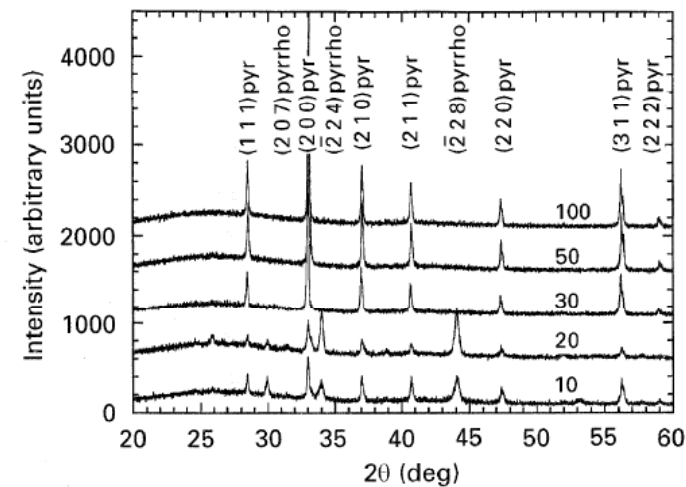
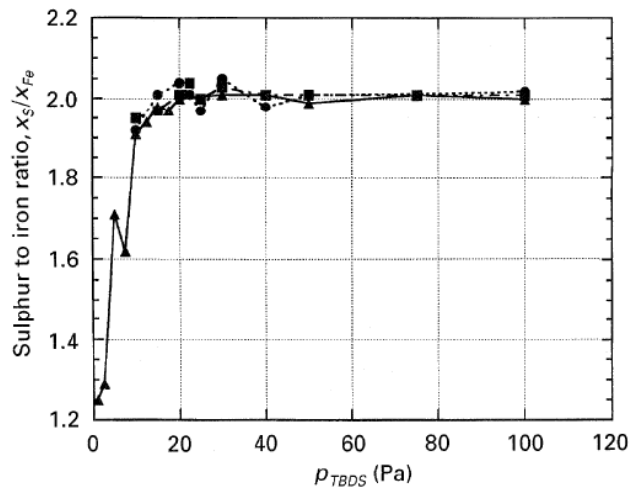
Evidence against it:

- **pyrite solar cells show large photocurrents (high EQEs)**
- TEM studies of single crystals show no phase or line defects
- the best pyrite films show S:Fe = 2.00 and no detectable impurities by XRD or magnetic susceptibility
- authors cherry pick the worst film preps (sol gel, sputter, spray pyro)

Conclusions?

Stoichiometry and properties of CVD films

Above a critical S pressure, LPCVD films are stoichiometric (2.0), phase pure (by XRD), and free of pyrrhotite (magnetism).

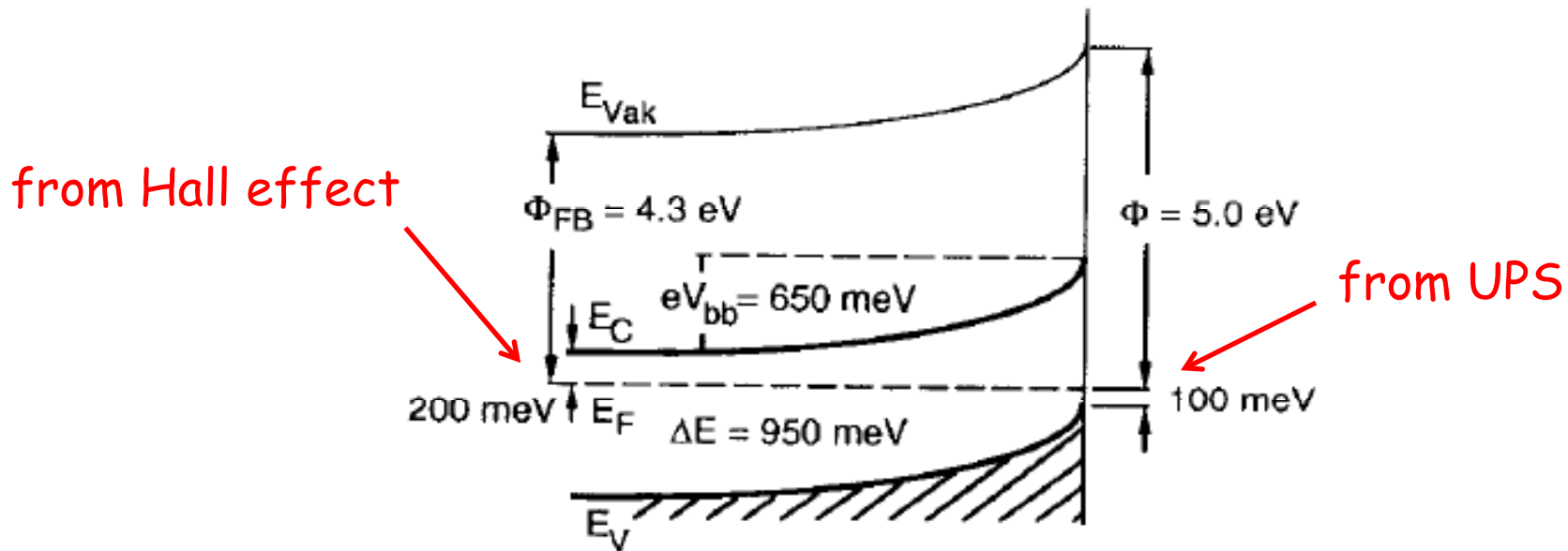


Hypothesis II: intrinsic surface states

Intrinsic surface states (square pyramidal Fe) pin the Fermi level at the valence band edge, which somehow reduces the photovoltage

Evidence for it:

inversion layer on *n*-type cleaved single crystal



Bronold, M., Tomm, Y., Jaegermann, W. *Surf. Sci.* **1994**, 314, L931.

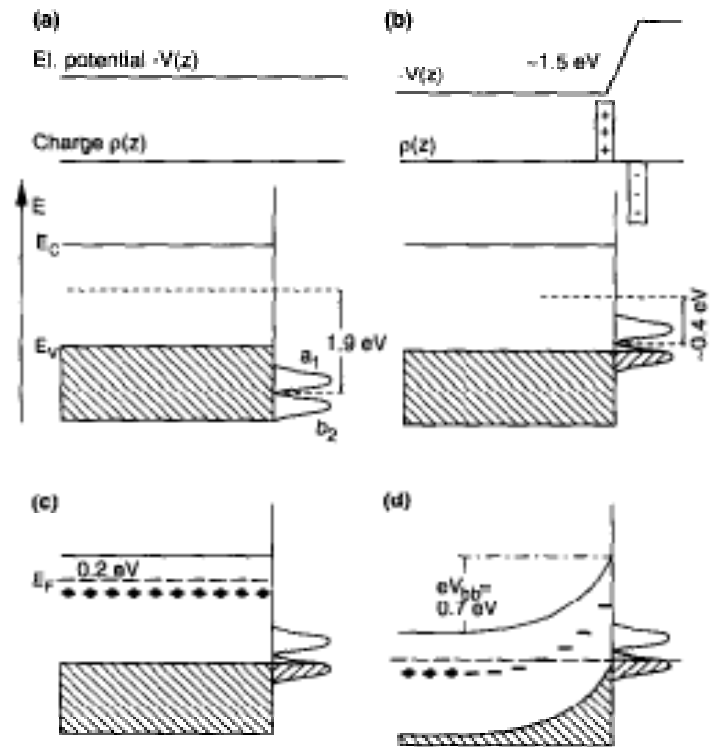
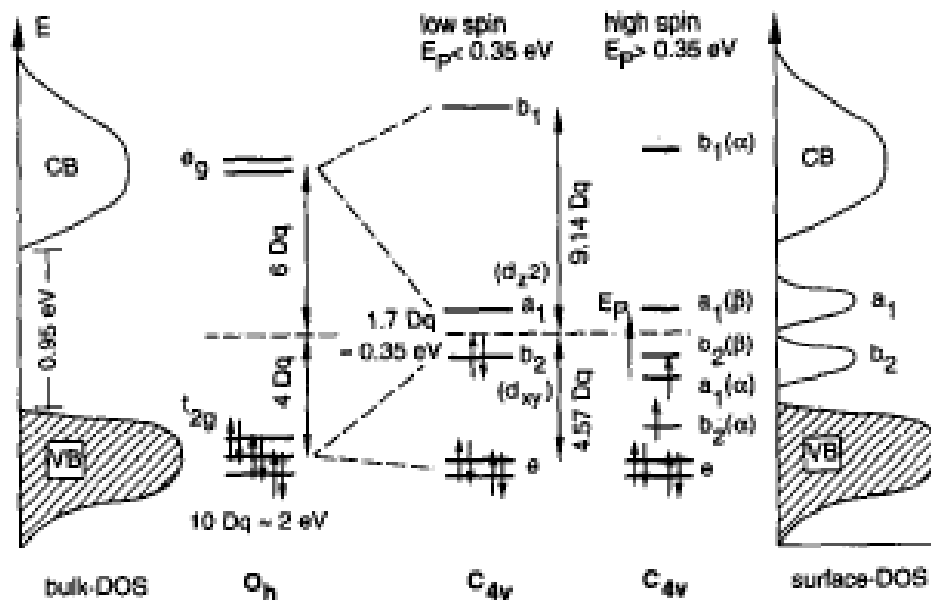
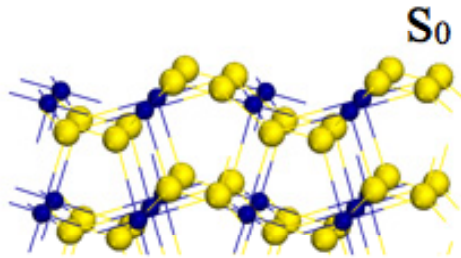
Birkholz, M. et al. *Phys. Rev. B* **1991**, 43, 11926.

Ellmer, K., Hopfner, C. *Phil. Mag. A* **1997**, 75, 1129.

$$V_{bb} = 650 \text{ mV}$$

Nature of the alleged intrinsic states

d_{z^2} and d_{xy} orbitals of 5-coordinate surface iron ions

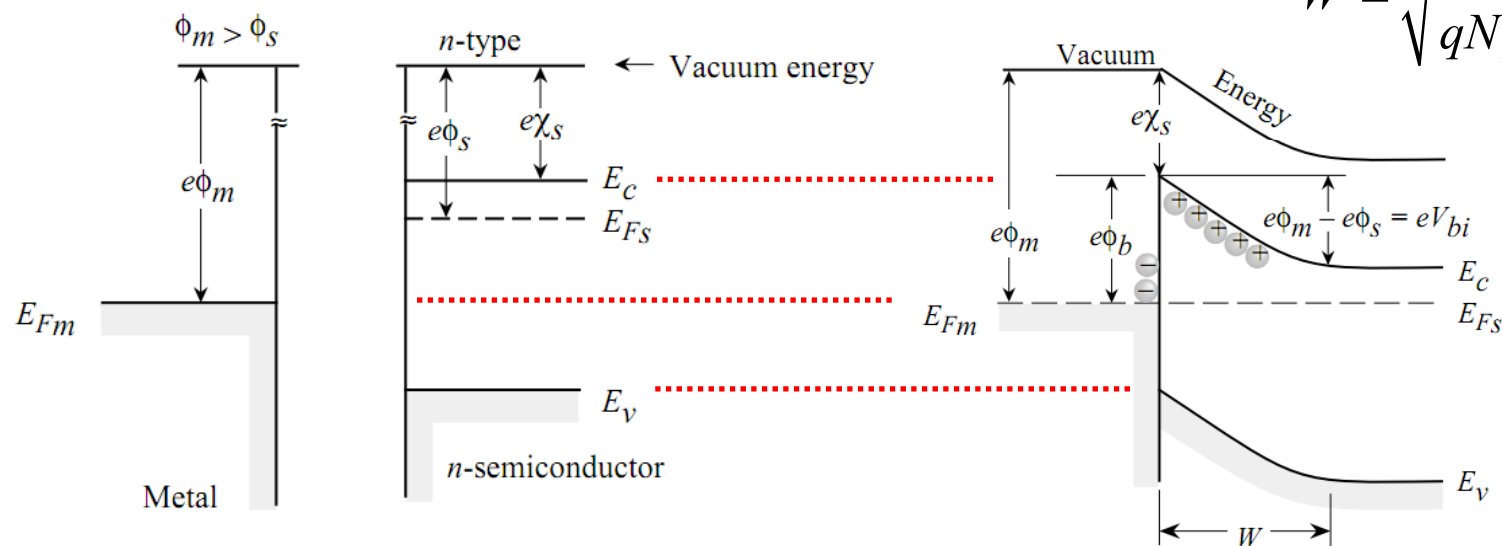


- Semi-quantitative ligand field theory puts the states near the VBM. Some DFT studies (including ours) agree.
- Recent MIT results (*PRB* 83, 235311) show no states in gap

What is Fermi level pinning?

Fermi level pinning: When surface states of a semiconductor cause a fixed amount of band bending, independent of any metal or other contacting phase

Schottky junction w/o pinning:



$$W = \sqrt{\frac{2\epsilon_s}{qN_A} \left(V_{bi} - V - \frac{kT}{q} \right)}$$

METAL-SEMICONDUCTOR JUNCTION AT EQUILIBRIUM

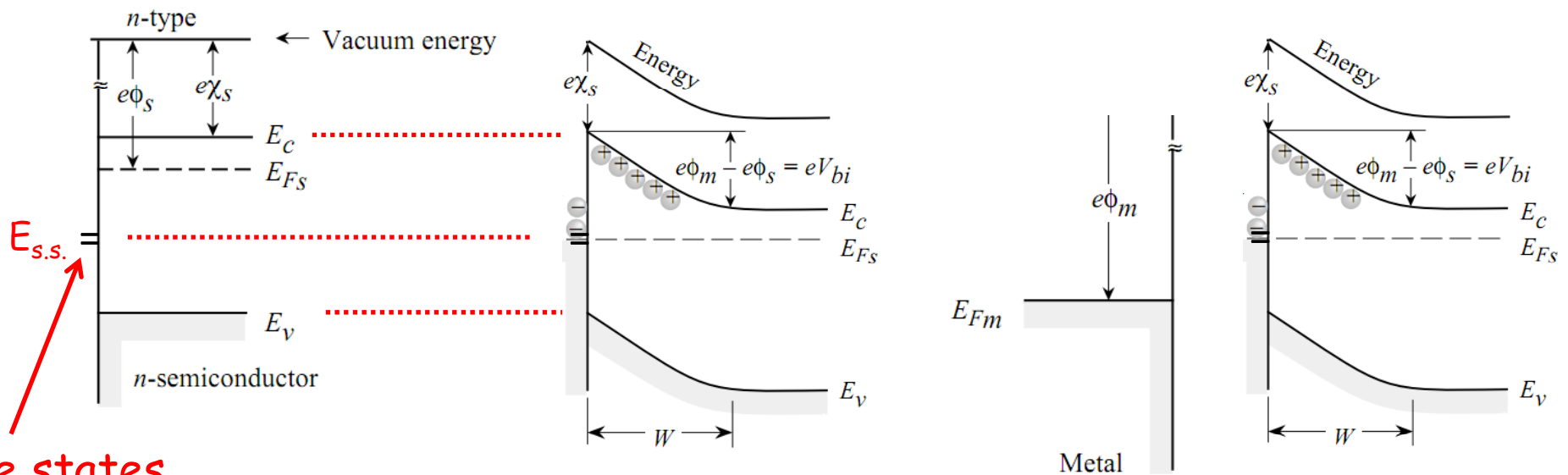
with no pinning:

$$V_{bi} = V_{bb} = \phi_m - \phi_s$$

*can maximize V_{bb} by using a metal with E_F close to VBM

What is Fermi level pinning?

Schottky junction with pinning:



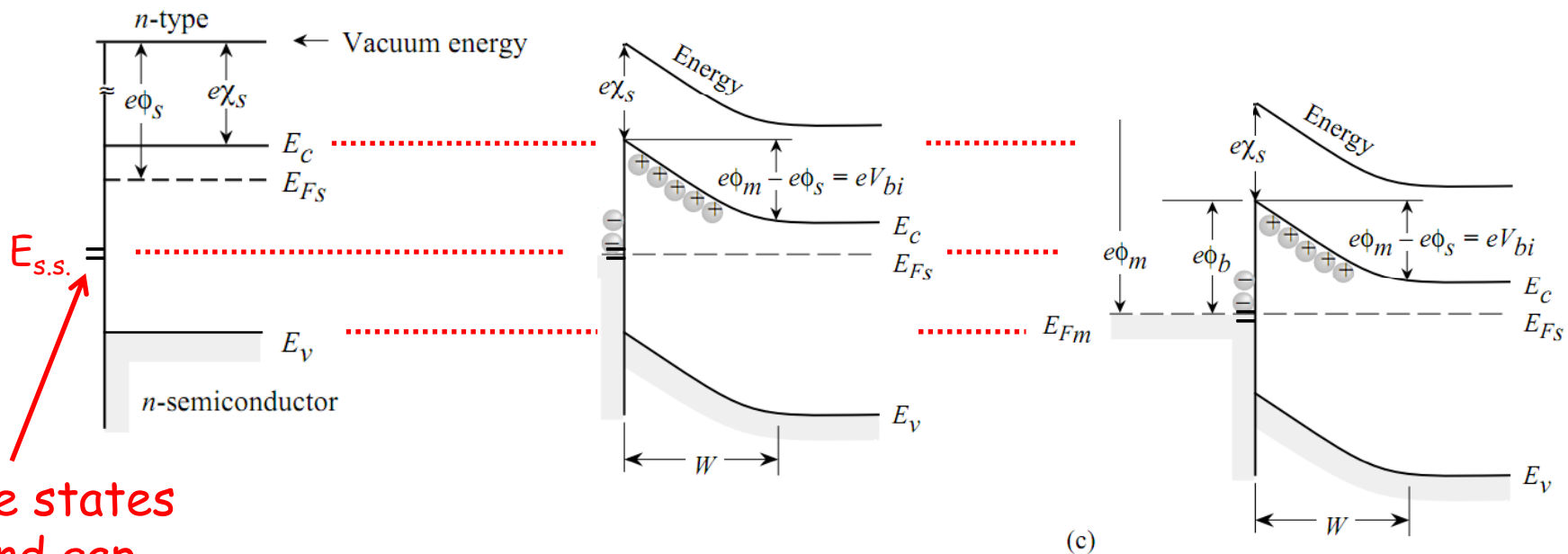
surface states
in band gap

with pinning:
$$V_{bb} = E_{s.s.} - \phi_s$$

* V_{bb} doesn't depend on metal because surface states act like a metal (reservoir of carriers)

What is Fermi level pinning?

Schottky junction with pinning:



surface states
in band gap

with pinning:
$$V_{bb} = E_{s.s.} - \phi_s$$

* V_{bb} doesn't depend on metal because surface states act like a metal

Consequences of Fermi level pinning

FL pinning controls the band bending and can be good or bad, depending on the energy of surface states and doping of SC.

Scheme II. Interface Energetics for an Ideal n-Type Semiconductor (Top) Contacting a Solution of A^+/A or B^+/B Showing Band Bending, E_V , Dependent on Position of E_{redox} While E_{VB} and E_{CB} Are Fixed. Interface Energetics for an n-Type Semiconductor Exhibiting Fermi Level Pinning (Bottom), Where E_V Is Independent of E_{redox} While E_{VB} and E_{CB} Shift Relative to Solution Levels

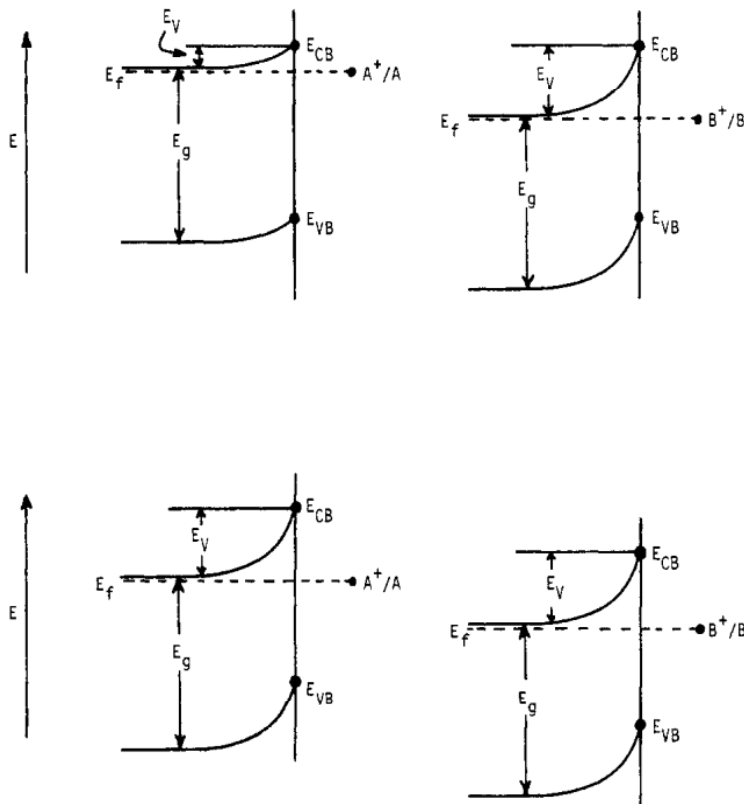


Table I. Semiconductor/Metal Interface Barrier Heights: “Fermi Level Pinning” at Solid-State Junctions^a

semiconductor	metal	T, K	barrier height, V
n-GaAs	Au	300	0.95 ± 0.03
	Pt	300	0.94 ± 0.03
	Be	300	0.82
	Ag	300	0.93 ± 0.03
	Cu	300	0.87 ± 0.03
	Al	300	0.80 ± 0.02
p-GaAs	Al	77	0.88 ± 0.04
	Au	300	0.48 ± 0.01
	Au	77	0.46
	Pt	77	0.48
	Ag	77	0.44
	Cu	77	0.52 ± 0.02
n-CdTe	Al	300	0.63 ± 0.06
	Al	77	0.61 ± 0.05
	Au	300	0.71 ± 0.02
	Pt	300	0.76
n-InP	Ag	300	0.81
	Au	300	0.49 ± 0.05
	Au	77	0.56 ± 0.04
	Cu	77	0.5
	Ag	300	0.54
	Ag	77	0.50

Consequences of Fermi level pinning

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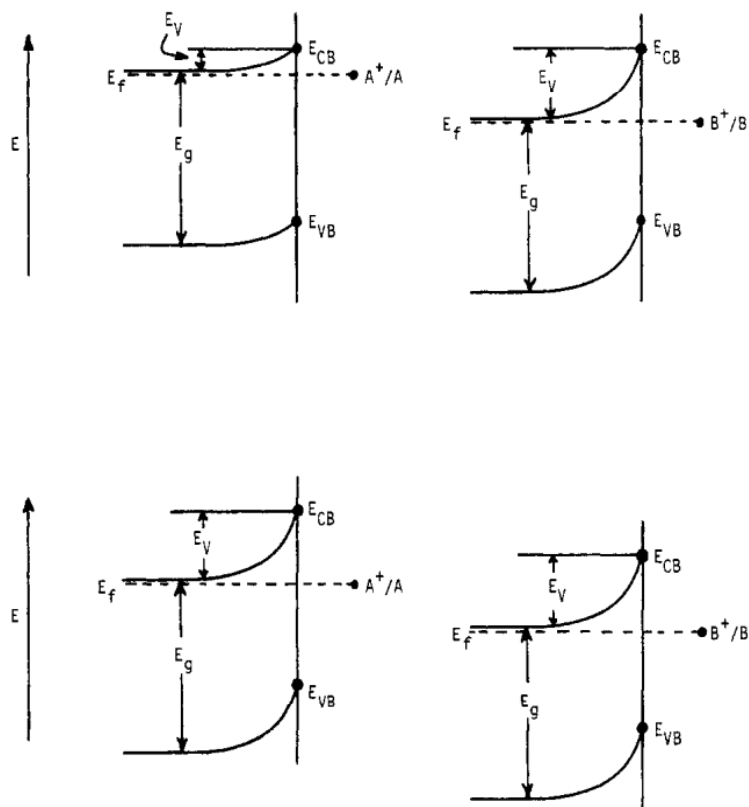
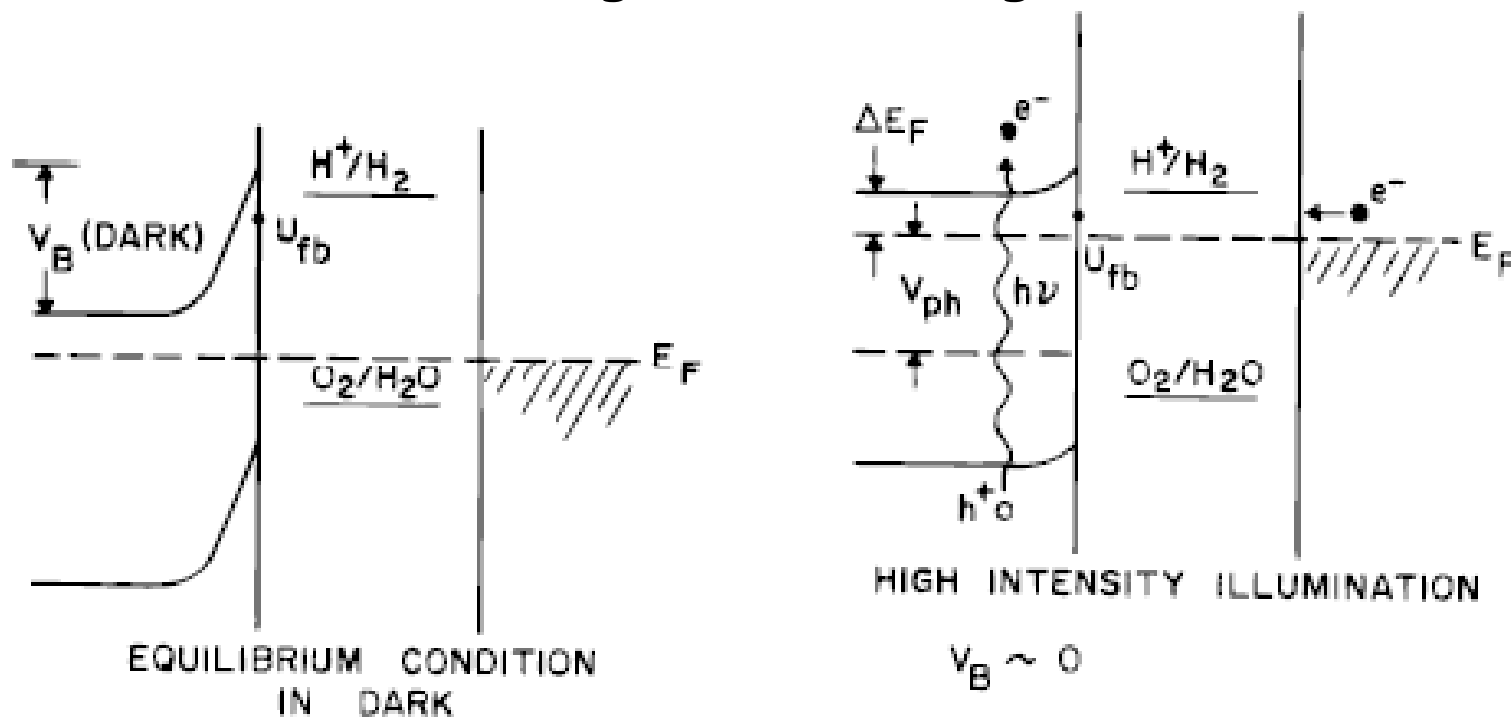


Table III. Semiconductor/Liquid Interfaces Where “Fermi Level Pinning” Applies^a

semiconductor (E_g , eV)	redox couple (E° , V vs. SCE)	photovoltage, V	ref
n-GaAs (1.35)	TMPD ⁺ /TMPD (0.1)	0.52	32
	Ox-1 ⁺ /Ox-1 (-0.42)	0.56	
	BQ/BQ ⁻ (-0.52)	0.46	
	AQ/AQ ⁻ (-0.94)	0.50	
	Ru(TPTZ) ₂ ^{3+/2+} (-0.81)	0.42	
	Ru(TPTZ) ₂ ^{2+/+} (-0.97)	0.41	
	Ru(TPTZ) ₂ ^{+/0} (-1.63)	0.29	
	Ru(TPTZ) ₂ ^{0/-} (-1.88)	0.24	
	Ru(bpy) ₃ ^{2+/+} (-1.30)	0.35	
	Ru(bpy) ₃ ^{+/0} (-1.49)	0.30	
	Ru(bpy) ₃ ^{0/-} (-1.73)	0.35	
	DPA/DPA ⁻ (-1.84)	0.43	
	A/A ⁻ (-1.94)	0.35	
p-GaAs (1.35)	TMPD ⁺ /TMPD (0.1)	0.02	32
	Ox-1 ⁺ /Ox-1 (-0.42)	0.12	
	AQ/AQ ⁻ (-0.94)	0.29	
	Ru(TPTZ) ₂ ^{3+/2+} (-0.81)	0.44	
	Ru(TPTZ) ₂ ^{2+/+} (-0.97)	0.44	
	Ru(TPTZ) ₂ ^{+/0} (-1.63)	0.56	
	Ru(TPTZ) ₂ ^{0/-} (-1.88)	0.61	
	Ru(bpy) ₃ ^{2+/+} (-1.30)	0.58	
	Ru(bpy) ₃ ^{+/0} (-1.49)	0.64	
	Ru(bpy) ₃ ^{0/-} (-1.73)	0.65	
	DPA/DPA ⁻ (-1.84)	0.25	
	A/A ⁻ (-1.94)	0.34	
	p-Si (1.1)	PQ ²⁺ /PQ ⁺ (-0.45)	
PO ⁺ /PQ ⁰ (-0.85)		0.42	
Ru(bpy) ₃ ^{2+/+} (-1.30)		0.42	
Ru(bpy) ₃ ^{+/0} (-1.49)		0.42	
Ru(bpy) ₃ ^{0/-} (-1.73)		0.38	

Band bending dictates maximum V_{OC}

The maximum open circuit voltage is equal to the amount of band bending (barrier height).

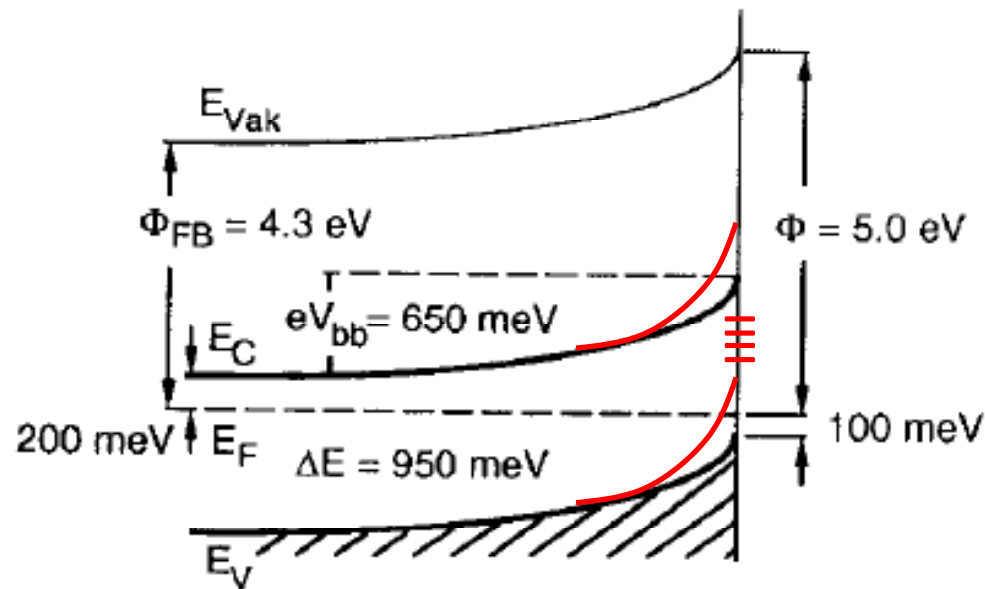


Illumination causes the bands to flatten.
Largest V_{OC} achieved when bands are flat.

$$(V_{OC})_{\max} = |V_{fb} - V_{redox}|$$

Back to hypothesis II

Pinning near the VBM should be helpful, giving a max voltage of ~650 mV. Actual voltage 0-200 mV. Why?

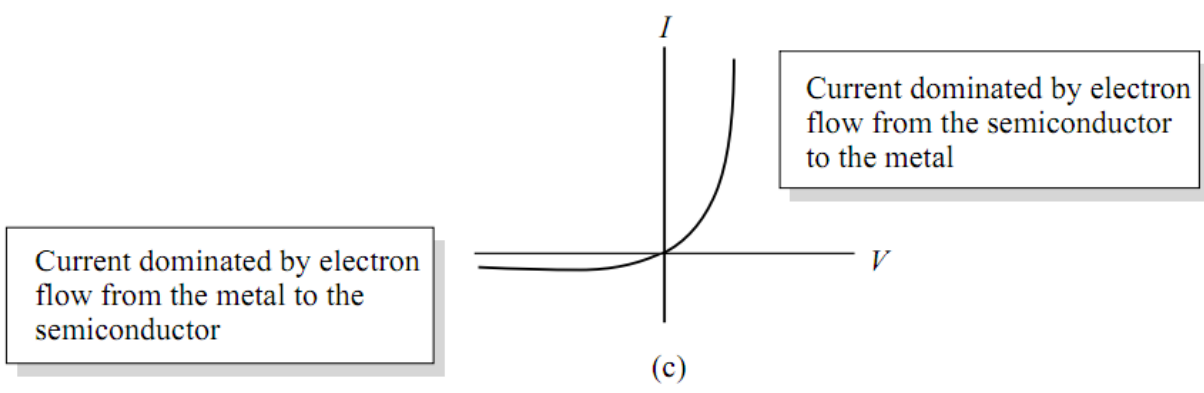
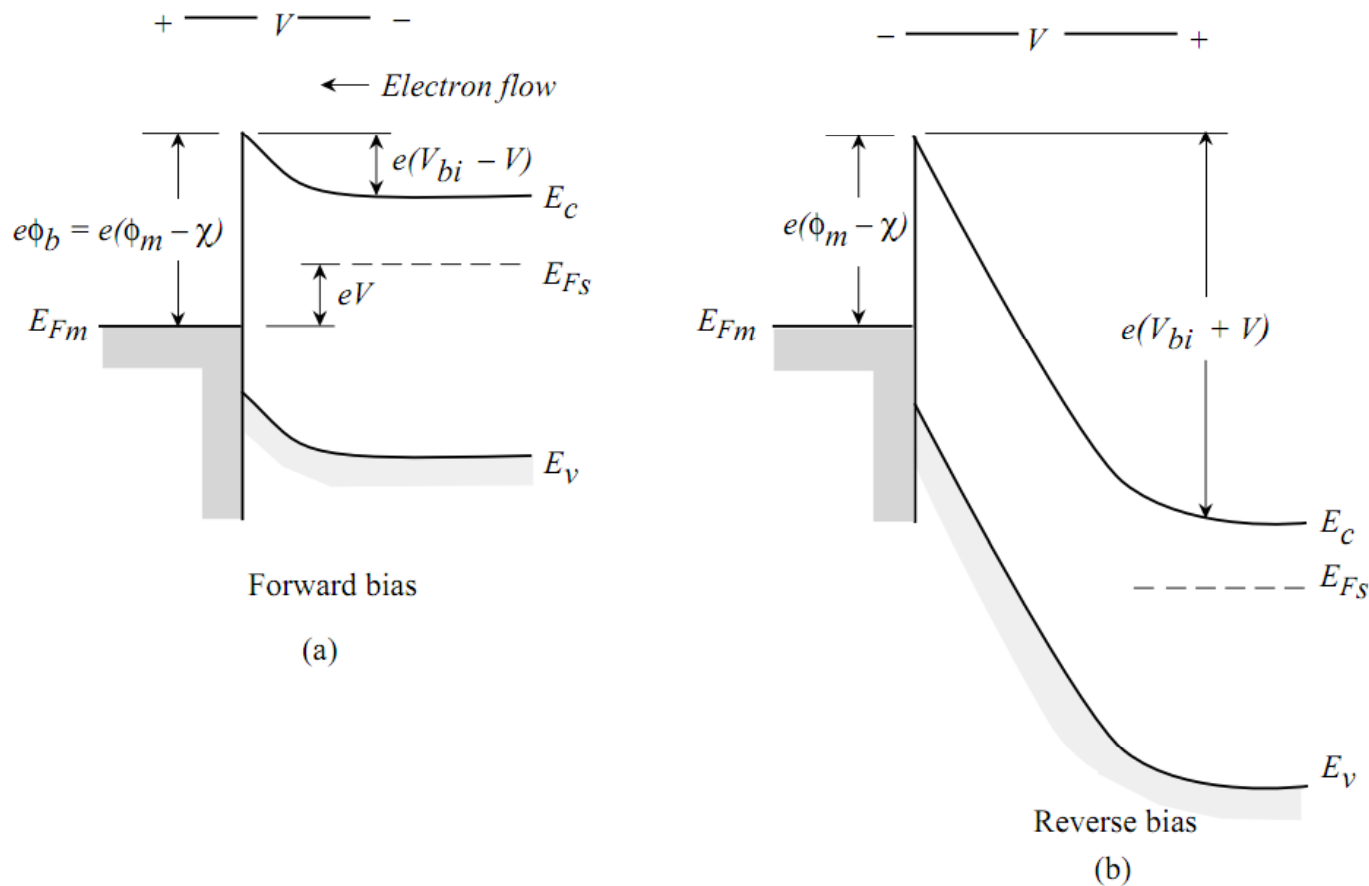


Pinning cannot by itself explain pyrite's low voltage.

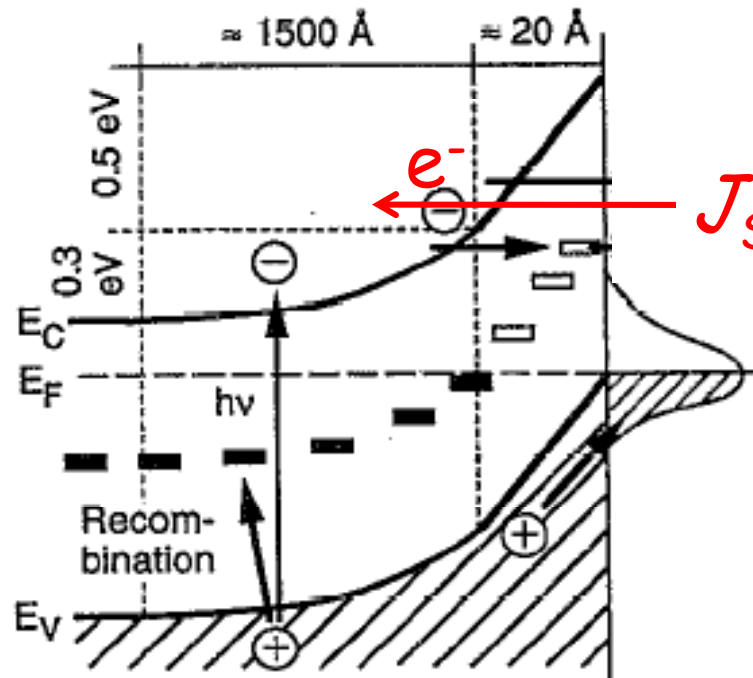
- Junction recombination is high (tunneling via s.s.?)
- Surface states are actually within VB or CB

→ Both should result in large reverse saturation current, low V_{OC} .

Schottky junction J-V curves



Reverse saturation current and V_{OC}



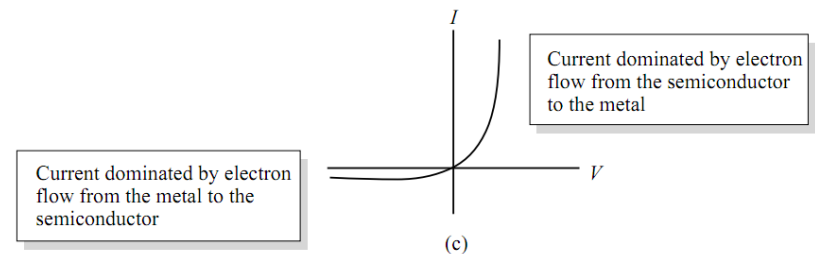
J_S (thermionic emission + tunneling)

dark:
$$J = J_S \left[\exp \frac{eV}{nkT} - 1 \right]$$

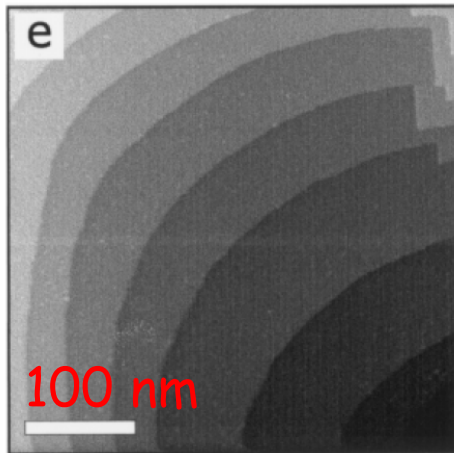
light:
$$J = J_S \left[\exp \frac{eV}{nkT} - 1 \right] - J_L \quad \rightarrow$$

$$V_{OC} = \frac{nkT}{e} \ln \left(\frac{J_L}{J_S} + 1 \right)$$

larger $J_S \rightarrow$ smaller V_{OC}

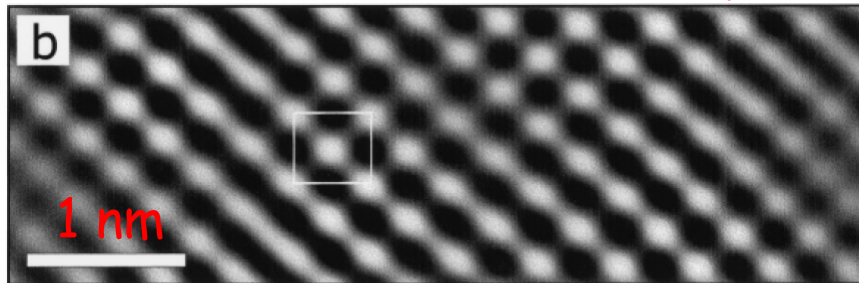


STM evidence for gap states

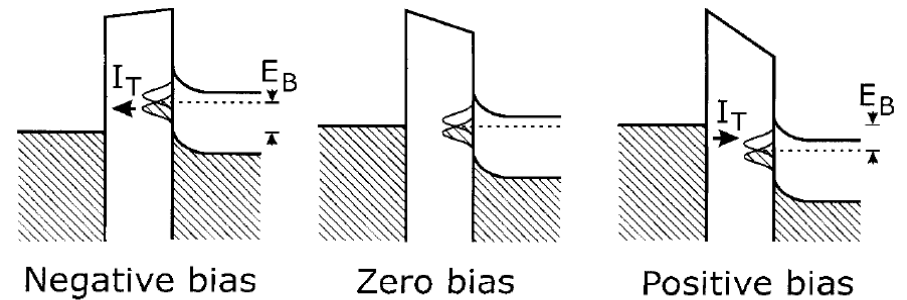
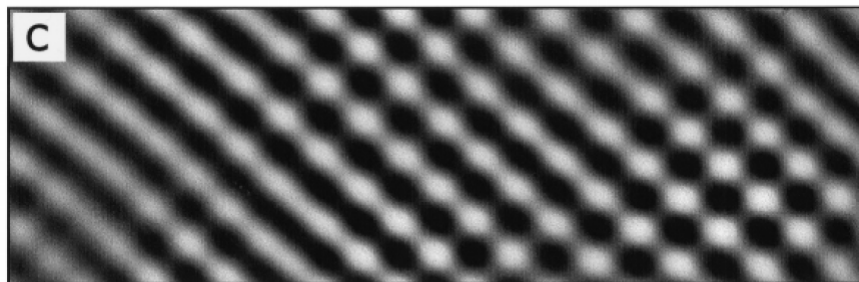


UHV cleaved
natural crystal

-0.14 V



+0.14 V

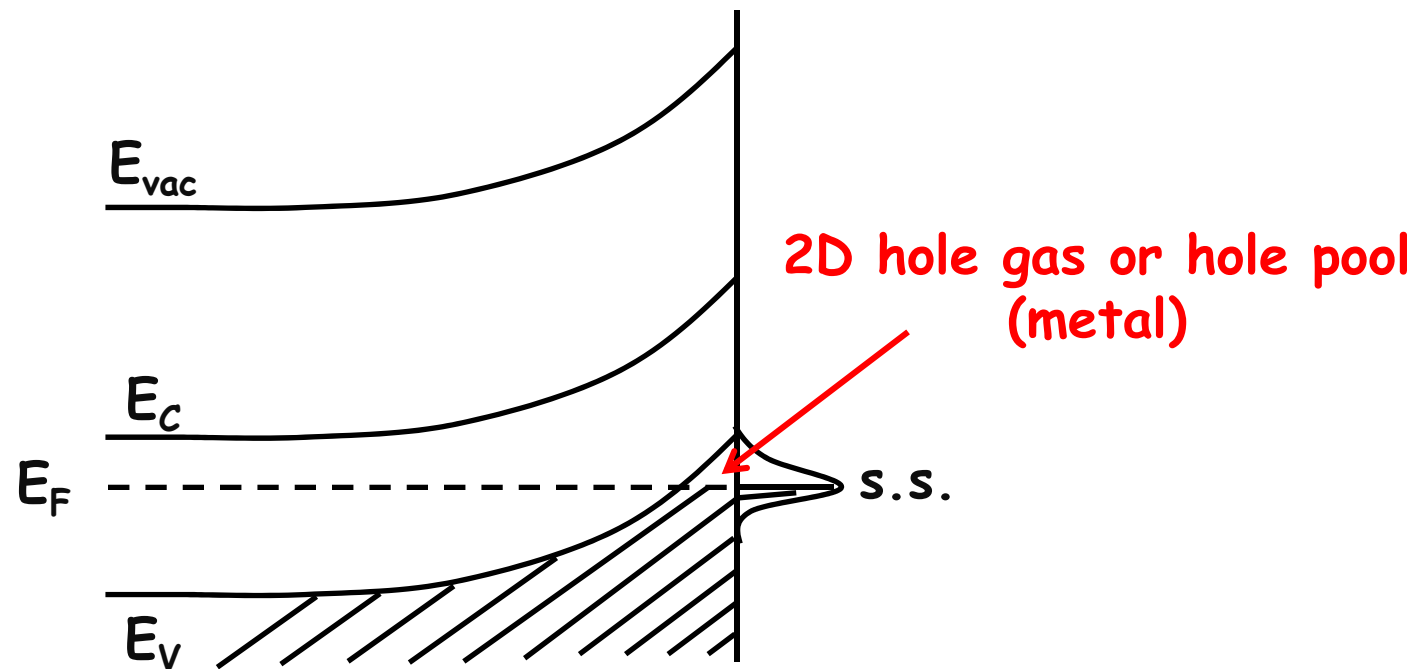


- Fe is both HOMO and LUMO
- surface gap is < 40 meV wide
- surface DOS seems continuous
- STM was “extremely difficult”
→ question robustness of results

Could also be explained by metallic
inversion layer

Metallic inversion layers

Surface states above the CBM or below the VBM can pin the Fermi level within a band, resulting in a metallic surface and small V_{OC}



Results in large dark current and minimal V_{OC}

Systems studied in the past

- *n*-type crystals cleaved in vacuum
- *n*-type crystals with Pt, Au, and Nb Schottky contacts (<300 mV)
- *n*-type crystals in contact with redox electrolytes (< 200 mV)

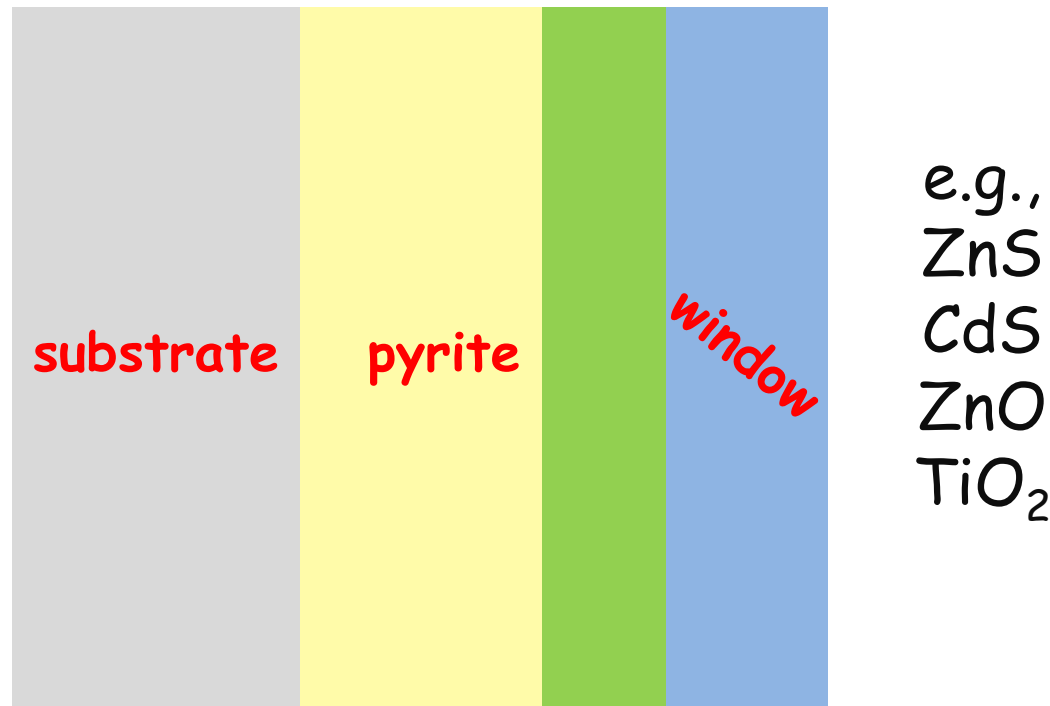
No photovoltages reported using *p*-type crystals!

Emerging picture

- Pyrite is a stoichiometric compound. Native defects (V_S , V_{Fe} , etc.) occur at less than 0.1-1% in the bulk.
- Native defects form more easily near the surface than in the bulk. Surface region may have a large defect density.
- Surface band gap is smaller than bulk band gap by at least 0.3 eV due to intrinsic and extrinsic surface states. Gap may even close for certain compositions. This is Hypothesis III: extrinsic defects
- Fermi level is pinned by surface states.
 - pinning in gap + tunneling through steep potential barrier can explain consistently low V_{OC}
 - pinning out of gap can be itself account for low V_{OC}

The way forward

If the pyrite surface is such a mess, just bury it.



Rapid thermal anneal:

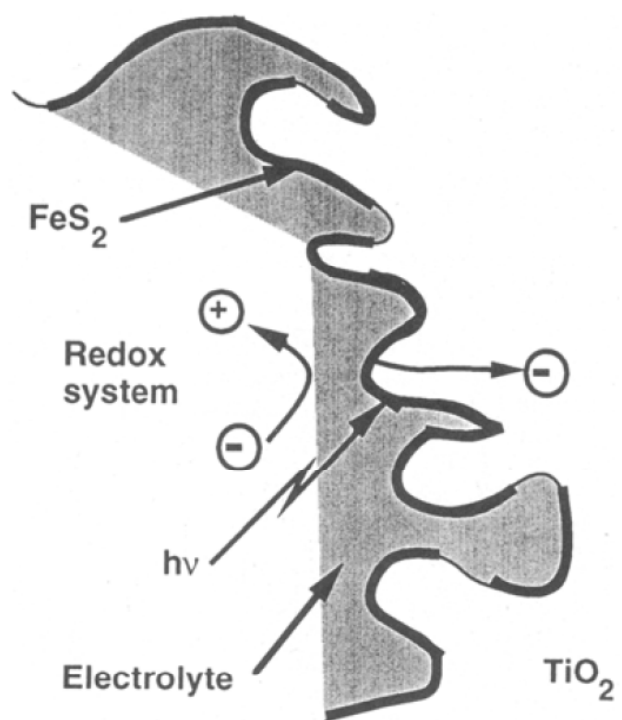
interlayer
(e.g., $Zn_xFe_{1-x}S_2$)

- eliminate defects and gap states
- grade the band gap
- form p-n junction

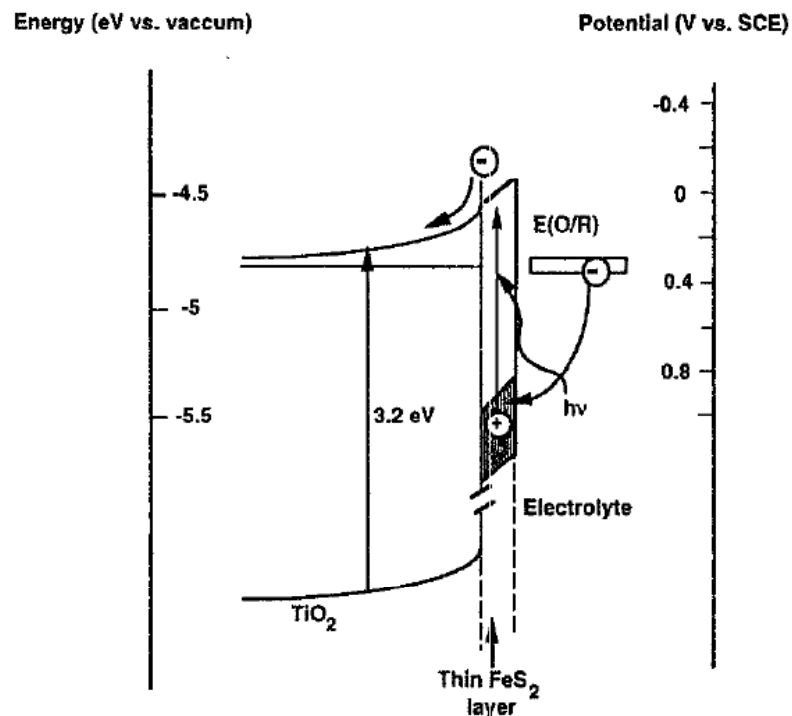
Pyrite-sensitized photoelectrochemical cells

Precedent for $\text{TiO}_2/\text{FeS}_2$

MOCVD pyrite on NCs



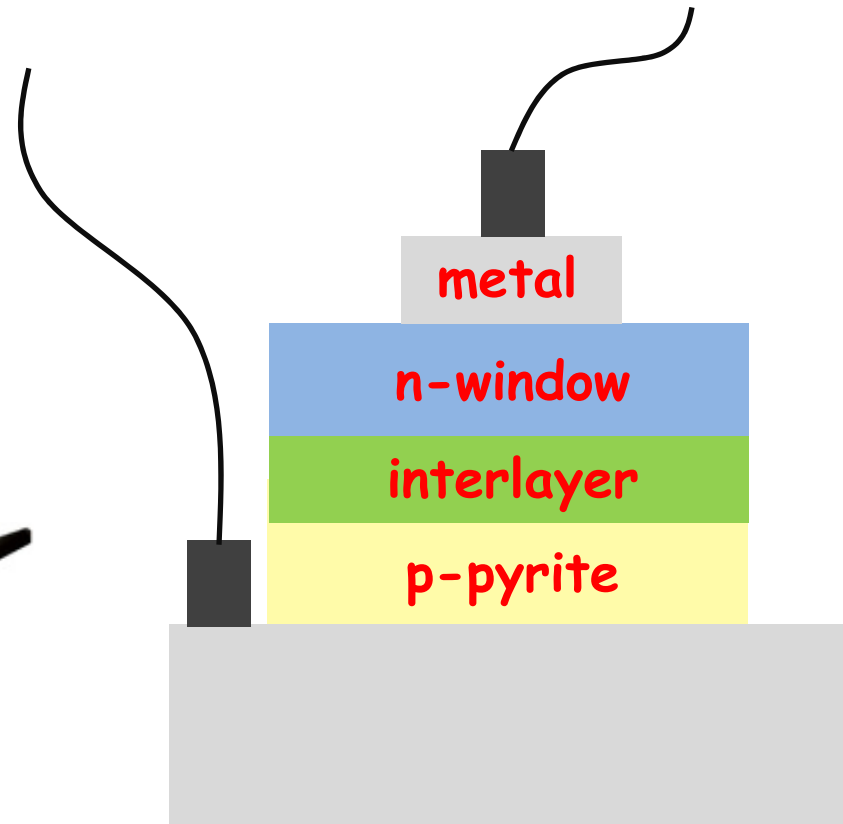
$0.5\text{M}/0.5\text{M} [\text{Fe}(\text{CN})_6]^{3-/4-}$



in acid: $J_{SC} = 6 \text{ mA cm}^{-2}$, $V_{OC} = 350 \text{ mV}$, **1%**
in base: $J_{SC} = 0.09 \text{ mA cm}^{-2}$, $V_{OC} = 600 \text{ mV}$

Otherwise, window layers have never been tried before

Focus of 2nd year effort: p-n junctions



- I-V measurements
- chemical analysis (UPS, SIMS)
- DFT calculations

New collaborations:

- **Wilson Ho (UCI): STM measurements on single crystals**
- **Sukgeun Choi (NREL): spectroscopic ellipsometry**
- **Craig Perkins (NREL): Auger microscopy, UPS, and SIMS**

END