

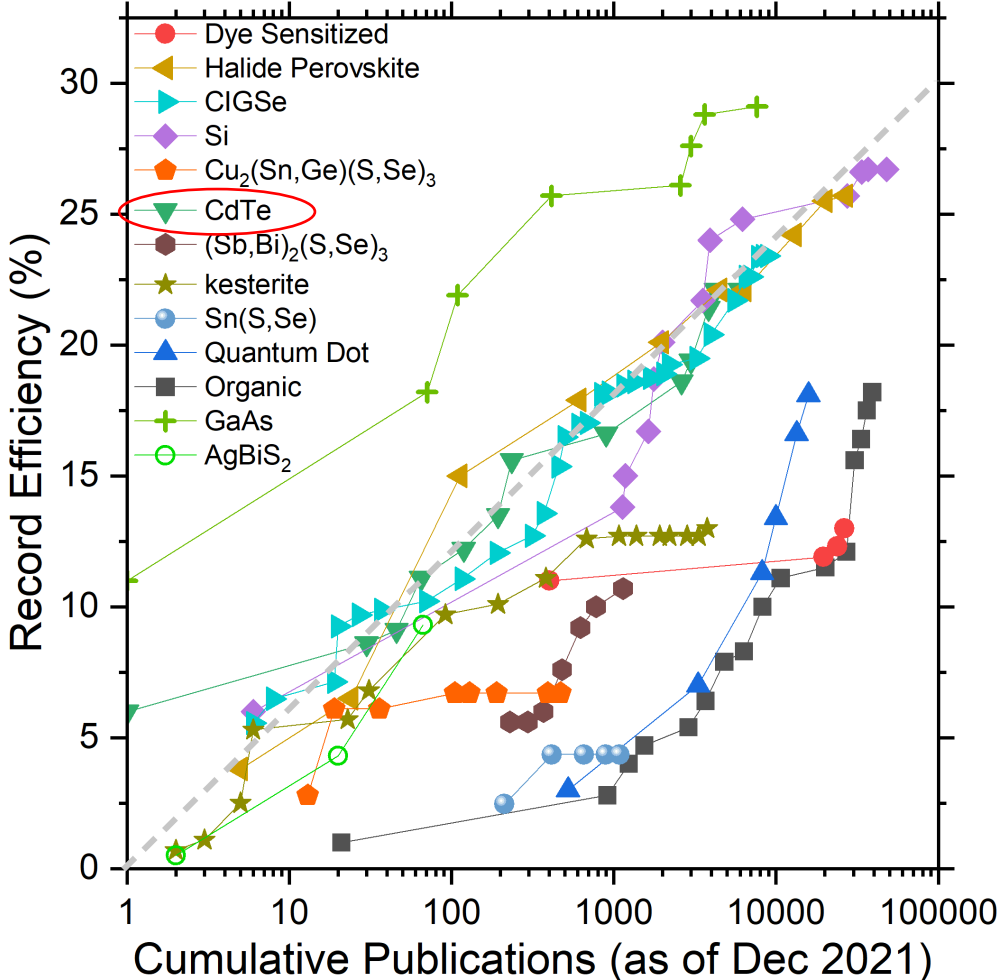


Surface
Photovoltage
Spectroscopy:
Shining New
Light on Back
Contacts

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Thank you to CSU, especially Amit Munshi for supplying cells
Thank you to 5N Plus for As-doped Se

Perspective: Efficiency vs Effort PV Technologies



Efficiency vs year hides many factors

Efficiency vs publications: analyze R&D effort it takes to improve different cell technologies.

CdTe, CIGSe, Si, and halide perovskites all fall on same curve!

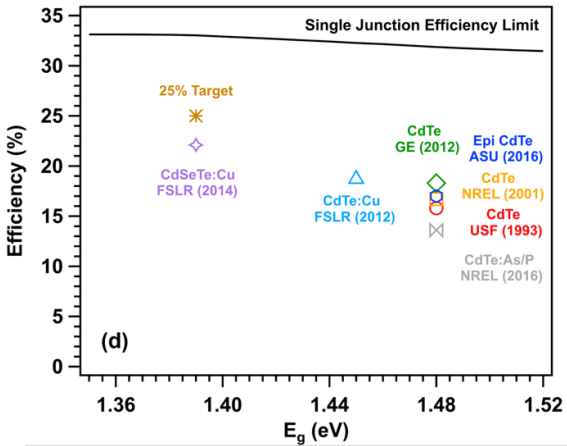
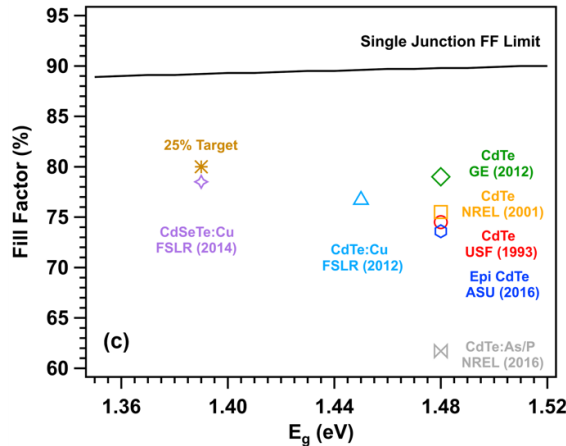
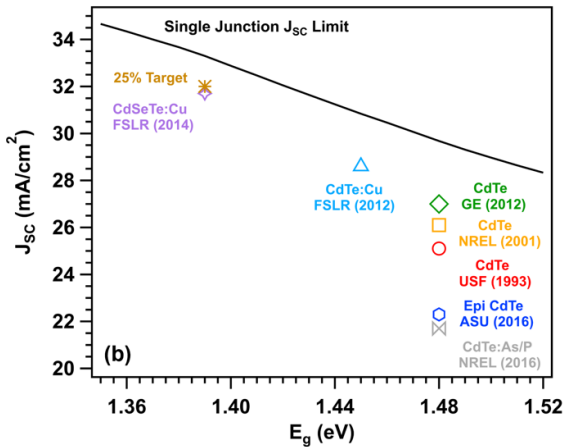
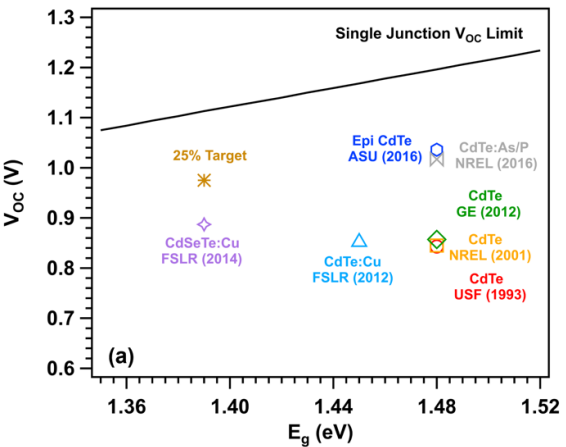
Efficiency is logarithmic with effort (is it all about recombination and V_{oc} ?)

Perovskites just had more people publishing

1 paper \approx 1 grad-student-year of effort \approx \$60,000 - \$100,000 ish



Path for CdTe: Improve V_{oc} and FF



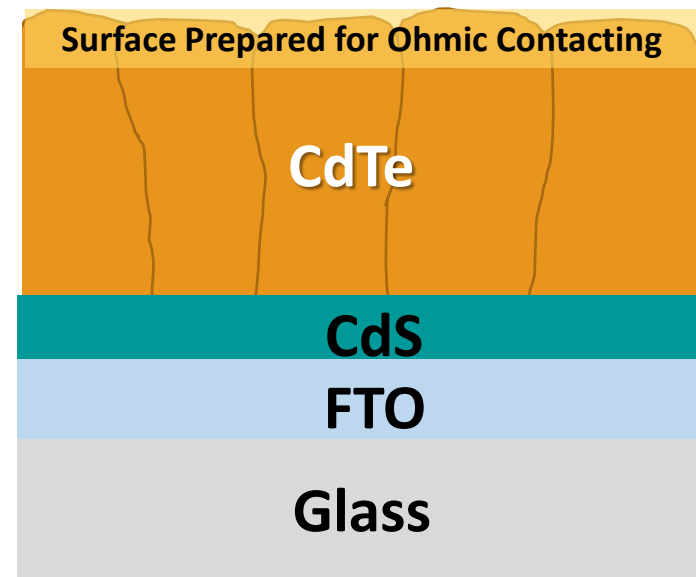
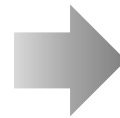
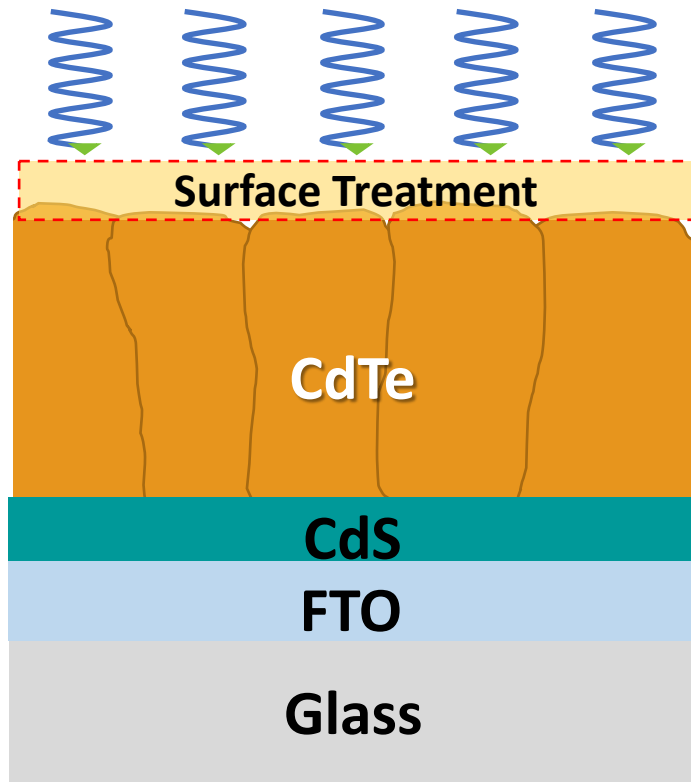
Origins of 900 mV V_{oc} ceiling ?

- Bulk & GB SRH
- Band tails (rad or nonrad recomb)
- Contact / interface recombination (maybe linked to band bending too)
- Contact carrier selectivity
- Contact V losses (energy offsets, $V=IR$)



Prior Work: Laser Enhanced Back Contacting

Concept: UV pulsed laser to modify surface



Simonds et al., JAP **116** 013506 (2014)

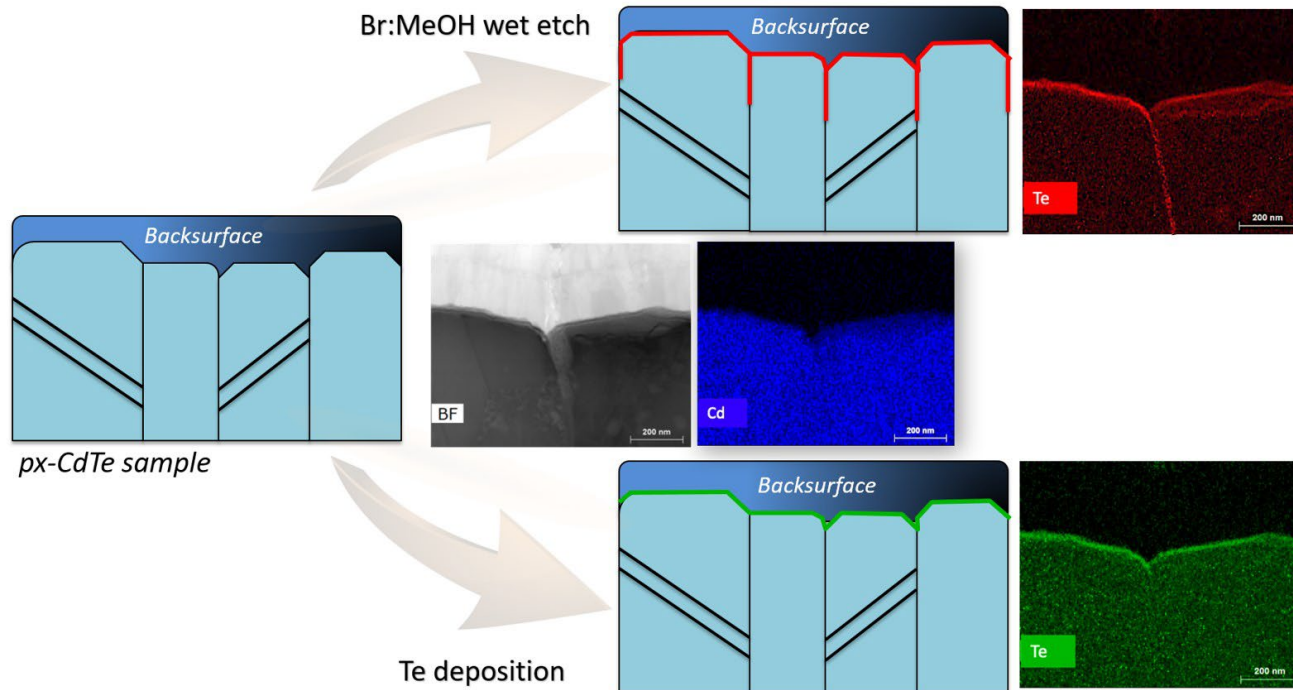
Simonds et al., APL **104** 141604 (2014)

Simonds, et al., J. Photonics for Energy Review (2014)

This was 10 yrs ago, not saying laser annealing is necessarily a solution now



Prior Work: GBs intersecting Back Contact



- Cd-selective etching leaves elemental Te in GBs (especially CSL boundaries)
- Narrow-gap Te in GB of CdTe limits device efficiency
- Solution: additive back contact processes like Te or ZnTe

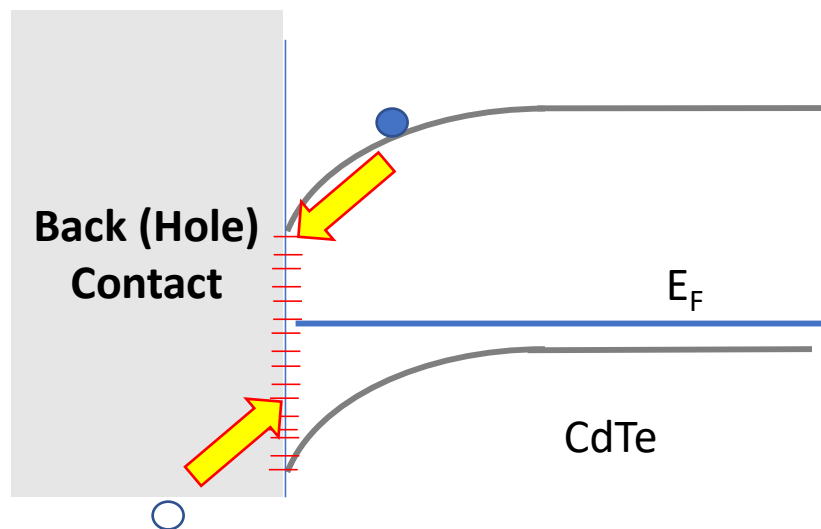


Want to Characterize Back Contact Properties

Want: Reversible, hole-selective, low-resistance, bifacial-enabling back contact

- Extract holes at E_{Fp} reversibly
 - Reject e^-
 - Suppress interface recombination
- Energy level alignment near V_{oc}
Upwards band bending (charge) or CB offsets
Passivate traps or keep e^- away

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Example of complex back contact situation

Donor-like traps at p-type contact:

- Definitely introduce SRV
- May also cause band bending in 10^{12} / cm^2 range

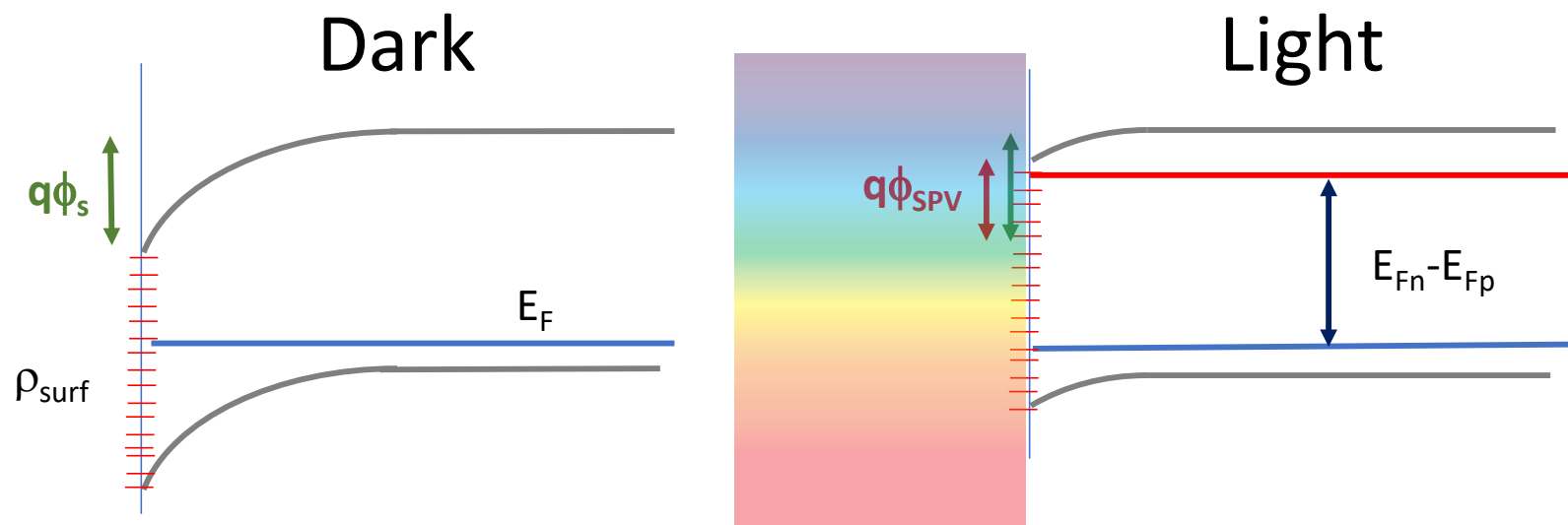
How to characterize?

Techniques for Advancing Back Contact Understanding

- Want to measure:
 - Band offsets / band bending
 - Surface states' charge
 - Surface states' recombination
- Backside IQE: effective surface recombination velocity (SRV)
- TRPL: effective surface recombination velocity (SRV)
- Surface photovoltage (SPV)
 - ✓ Band offsets / band bending
 - ✓ Surface states' charge
 - ✓ Surface states' recombination



Surface Photovoltage (SPV)



CdTe surface with E_F pinning from traps
 ϕ_s = surface built-in voltage

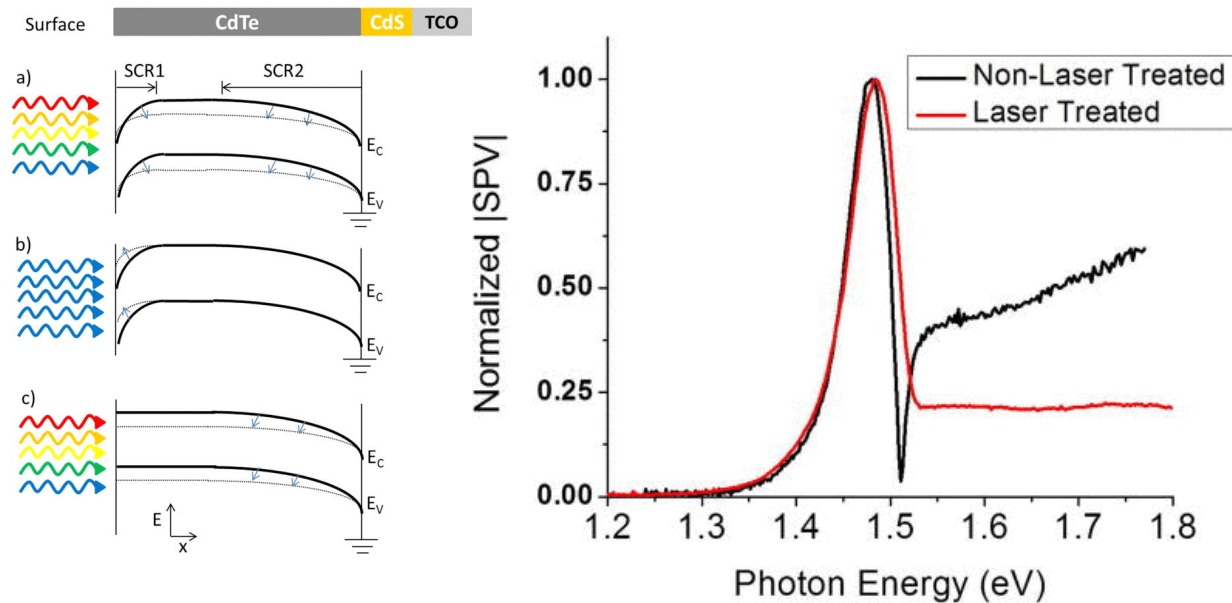
Excess carriers bias surface/bulk junction
towards flatband

ϕ_{SPV} magnitude depends on:

$\phi_s, \tau_{bulk}, \mu_{bulk}, SRV, \rho_{surf}, I_{light}(\lambda, t), \dots$

- SPV: same origin and physics as PV operation. Thus sensitive to all the same factors
- Can be used like IQE, but at V_{oc} rather than J_{sc}
- Adds some orthogonal information to JV, IQE, CV, etc
- Scalable, parallelizable, ...

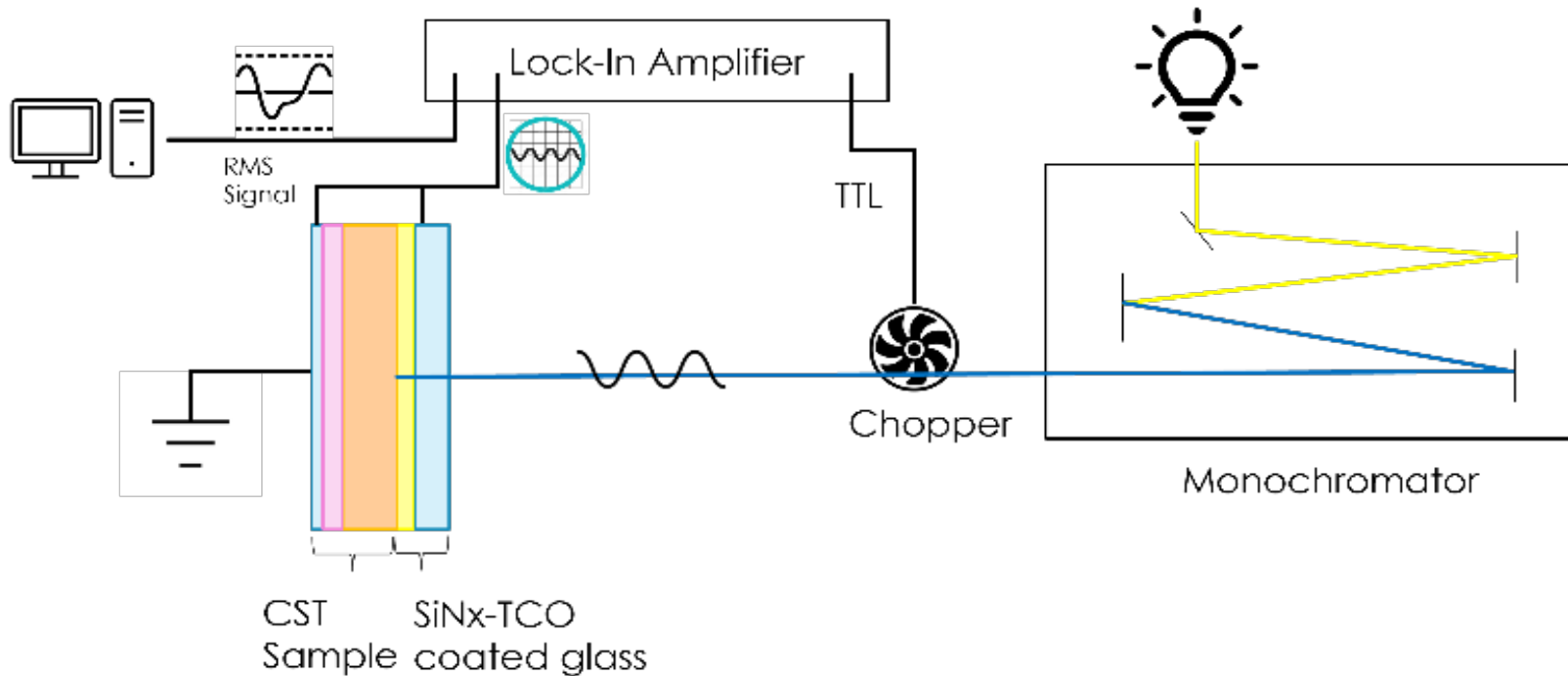
Prior Work: SPV Response to Laser Annealing



- 2014: we used surface photovoltage spectroscopy (SPS) to assess back surfaces
- SPS revealed laser annealing reduced back surface Fermi level pinning
- $h\nu = E_g$ probes whole cell; $h\nu > E_g$ above gap probes near-surface

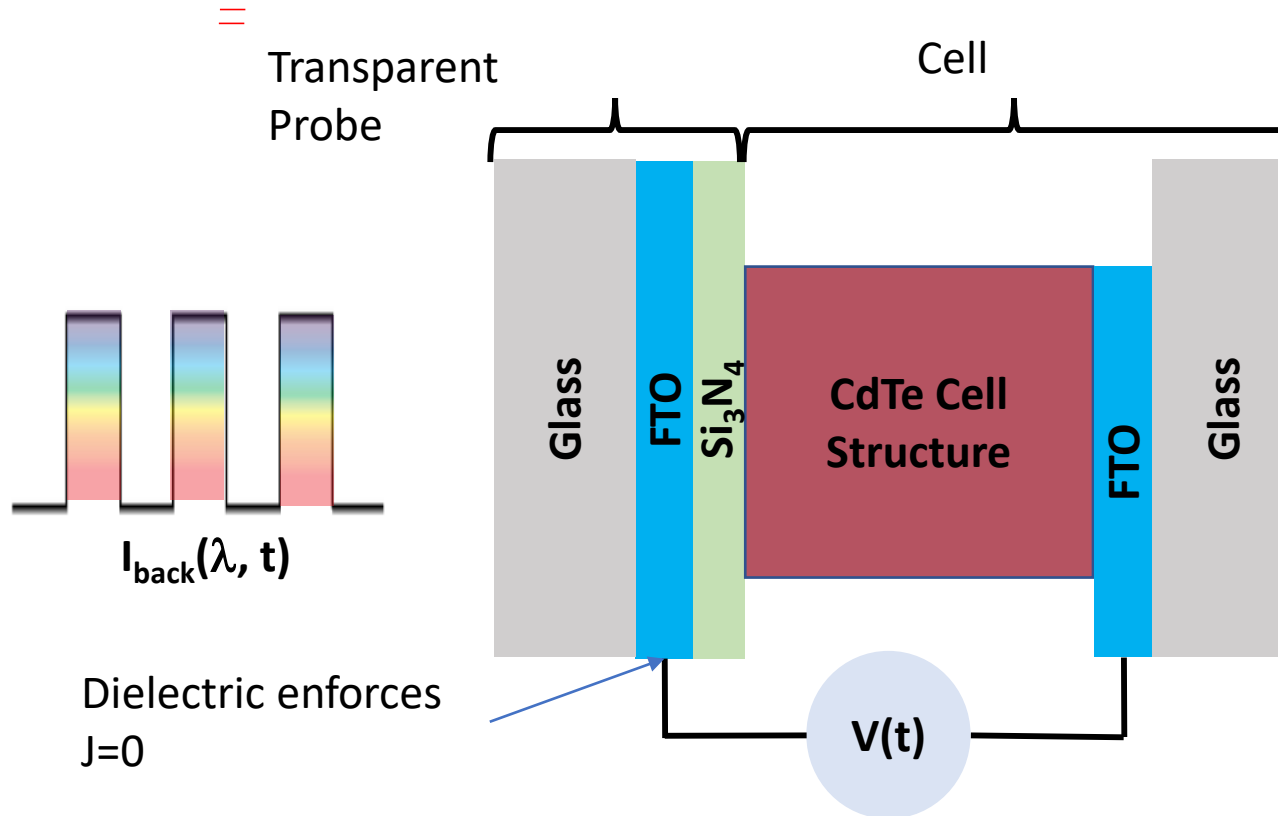


Current Set-Up



- Chopped monochromatic light (can add other sources and AM1.5 bias light)
- Create MIS structure between cell and SPV/SPS electrode (air or dielectric)
- Vary V and light during experiments
- Many ways to implement

Custom SPV/SPS Electrodes



- Custom electrode – SiN_x on FTO
- Good current blocking, easier alignment than air gap, better coupling
- Can send in light from either side to learn more

SPS Case Studies

Br:MeOH etching test

- Br:MeOH etch enhances our backside PL Passivation? E_F pinning/band bending?

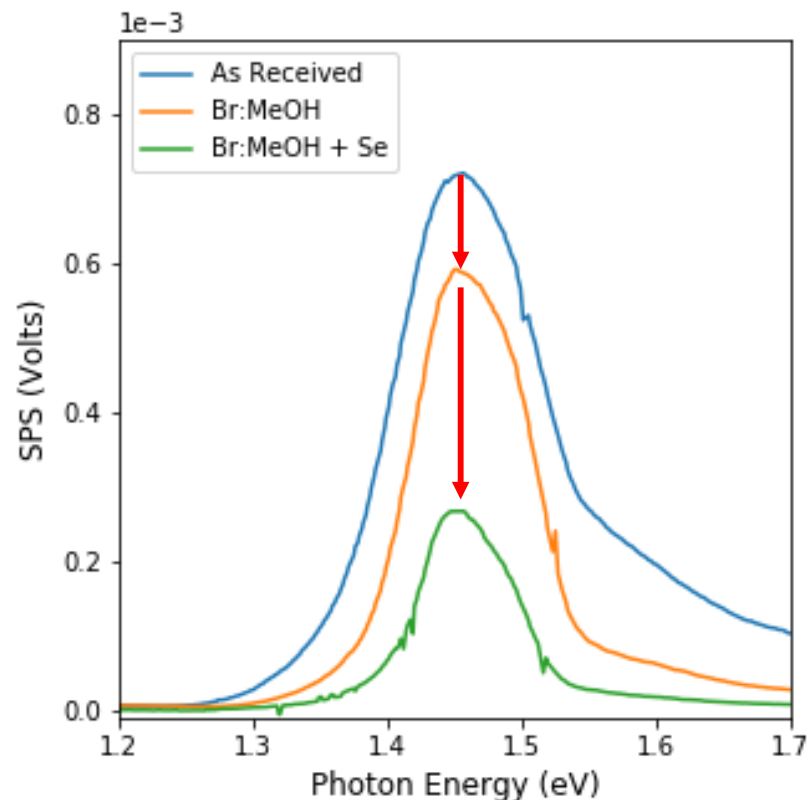
SPV decreases. Reduced SRV should increase it
 \therefore Reduction in E_F pinning dominates

Se to replace Te ?

- $E_g > 1.7$ eV, potentially electron reflecting
- Need p-type – tried As doping (5N Plus)
- Too insulating for good IV! As doping didn't work

SPV again decreased

\therefore Increase of SRV or decrease in E_F pinning (needs follow-up)



Takeaway: SPV sensitive to surface defect charge in these cases

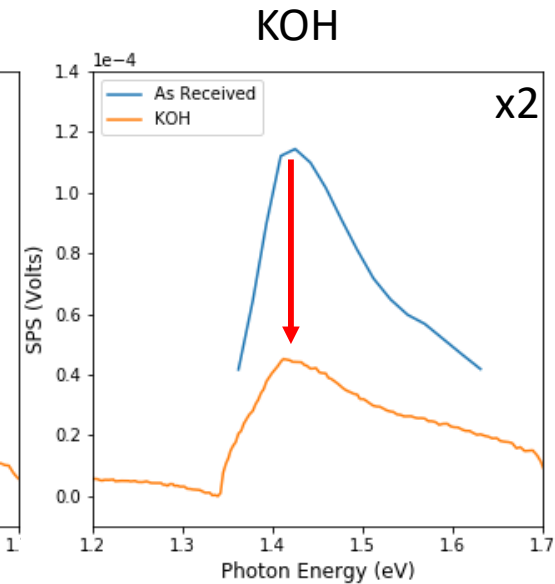
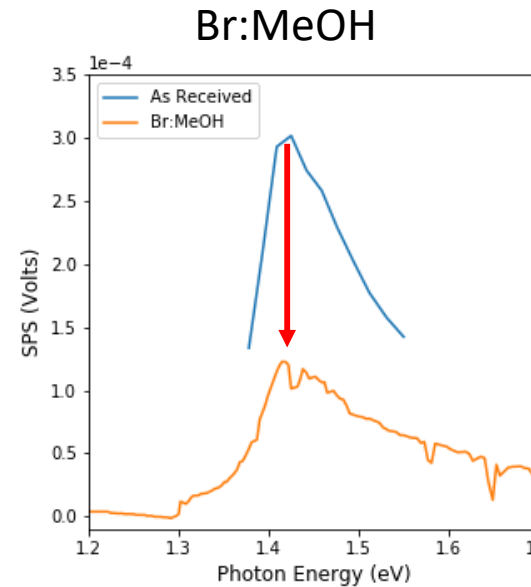
SPV: Provides Info Complimentary to TRPL

Reese (2015) SRV from TRPL

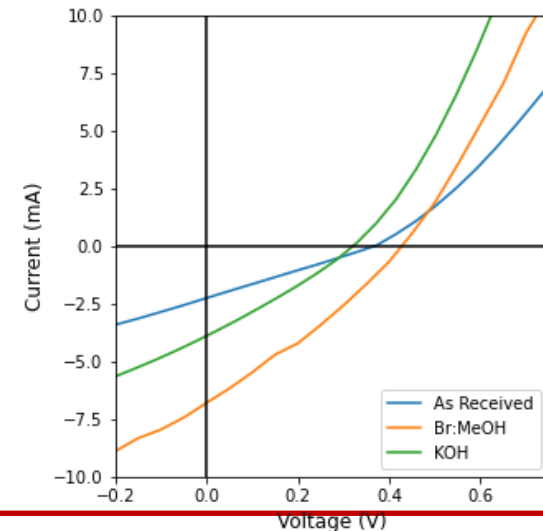
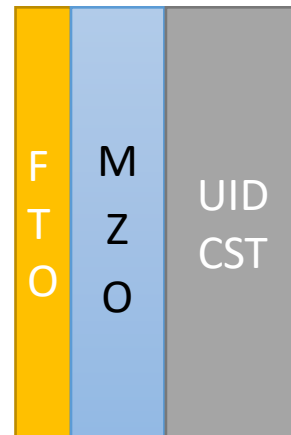
Untreated: $3-15 \times 10^5$ cm/s

KOH: 4×10^4 cm/s

Br-MeOH: 3×10^5 cm/s



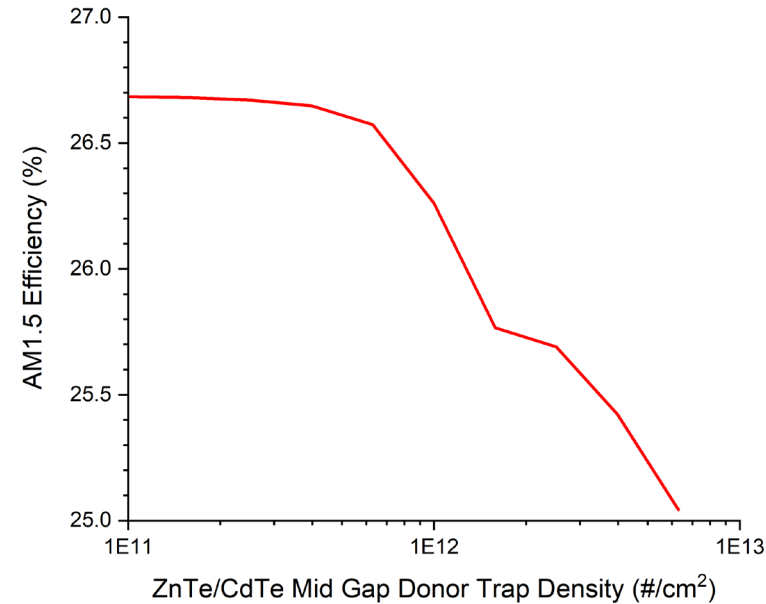
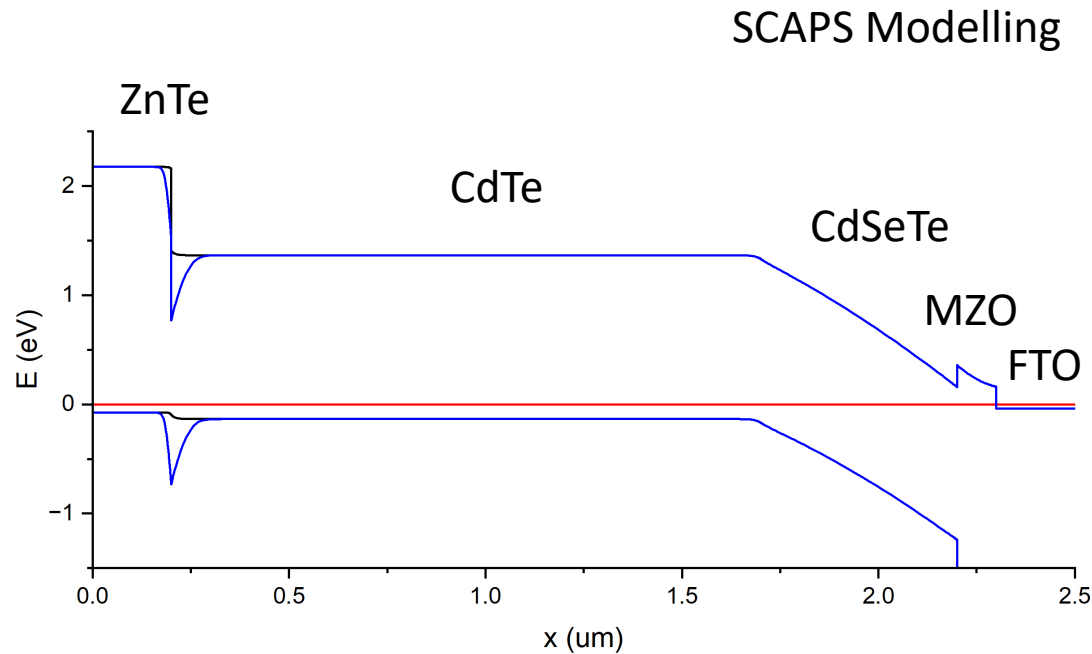
SPS again detects decreases in E_F pinning



*Why bad IV? Undoped CdSeTe cell



Example: Hypothetical Trap Charge at ZnTe/CdTe Interface



ZnTe/CdTe interface believed to be NOT passivated

- Treating interface as SRV misses the effect of defect charge; sufficiently-high trap density pins E_f and creates band bending
- As thickness \downarrow , minority carrier diffusion length \uparrow , and for bifacial operation, E_f pinning and SRV must decrease



Charge, Band Offsets, and Traps All Matter




- How are we modeling traps at interfaces and SRV?
 - Boundary condition?
 - Neutral SRH traps?
 - Traps having both charge and capture/emission?
- Effective SRV depends on band bending near traps (BSF in Si)

$$S_{eff} = S_{if} \cdot \exp\left(-q\phi_{if}/k_B T\right)$$

- Combining SPV, TRPL, IV, IQE... with modelling
- Each technique has some linear independence from others, thus combination can decouple parameters



What's Next?

- Better cells:
 - So far used sub-optimal cells – UID, poor surface quality, aged
 - Need high carrier concentration and bulk lifetime to correlate SPS to V_{oc}
- Bias light: 
 - Band bending depends on carrier injection
 - Apply bias light near AM1.5 to study interface near operating conditions
- Temperature dependence 
 - SPV signal exponentially dependent on intrinsic carrier concentration
- Monochromatic high intensity – super band gap LED or laser
- Frequency response 
 - MHz or GHz LED pulse
 - Sweep several orders of magnitude frequency response
 - Probe trap state lifetimes

Conclusions

- SPV is uniquely suited to evaluate rear contact strategies
 - Easy to set up
 - Probe interface or free surface
 - Measure potential barriers and trap states
- We have shown sensitivity to known effective wet etchants
- We show sensitivity to CdTe/passivation layer interface
- Interfaces affected by SRV, band bending, ultimately by the charge and density of traps
- SPV is complimentary measurement to TRPL to study all parameters which affect interfaces



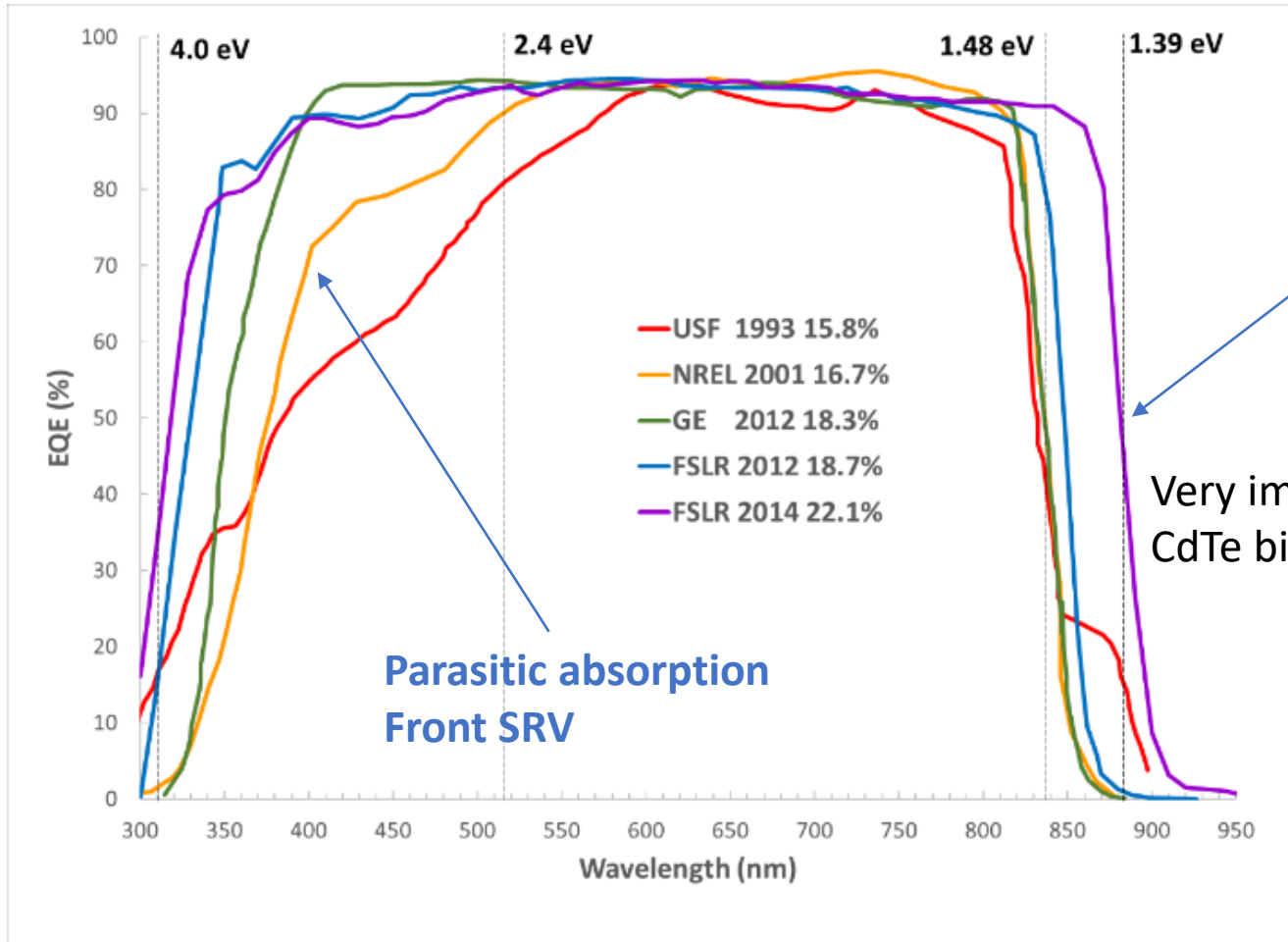


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IQE: Great for J_{sc}



Figure; SEMSC Review, forthcoming

Correlating Peak SPV to Recombination Velocity

- IV improvement shows overall positive effect
- But if SRV \downarrow SPV should \uparrow
- Effective SRV dependent on modeling
 - Neutral vs charged defects, number, cross section
- In presence of band bending induced by the traps themselves, SRV is multiplied by an $\exp(-\phi/V_{th})$ term

$$S_{eff} = S_{if} \cdot \exp\left(-\frac{q\phi_{if}}{k_B T}\right)$$

- Upward bending for e⁻ suppresses effective SRV but downward enhances it
- Br:MeOH/KOH decrease traps \rightarrow unpin Fermi level \rightarrow decreasing band bending \rightarrow decreasing SPV

