

# Junction Evolution During Fabrication of CdS/CdTe Thin-film PV Solar Cells

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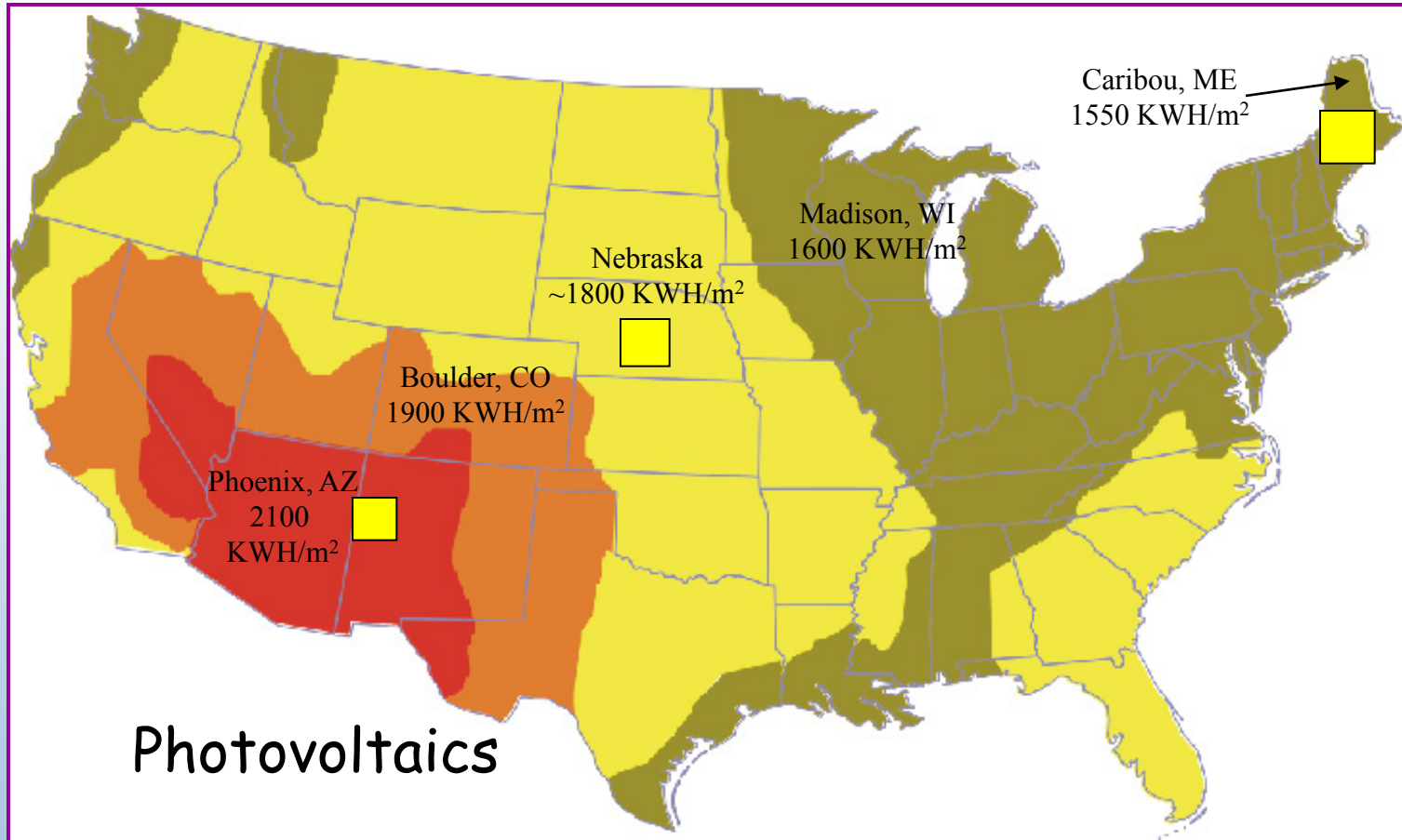
**NREL/PR-520-49387**

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# Solar Land Area Requirements For 2004 US Electricity Requirements



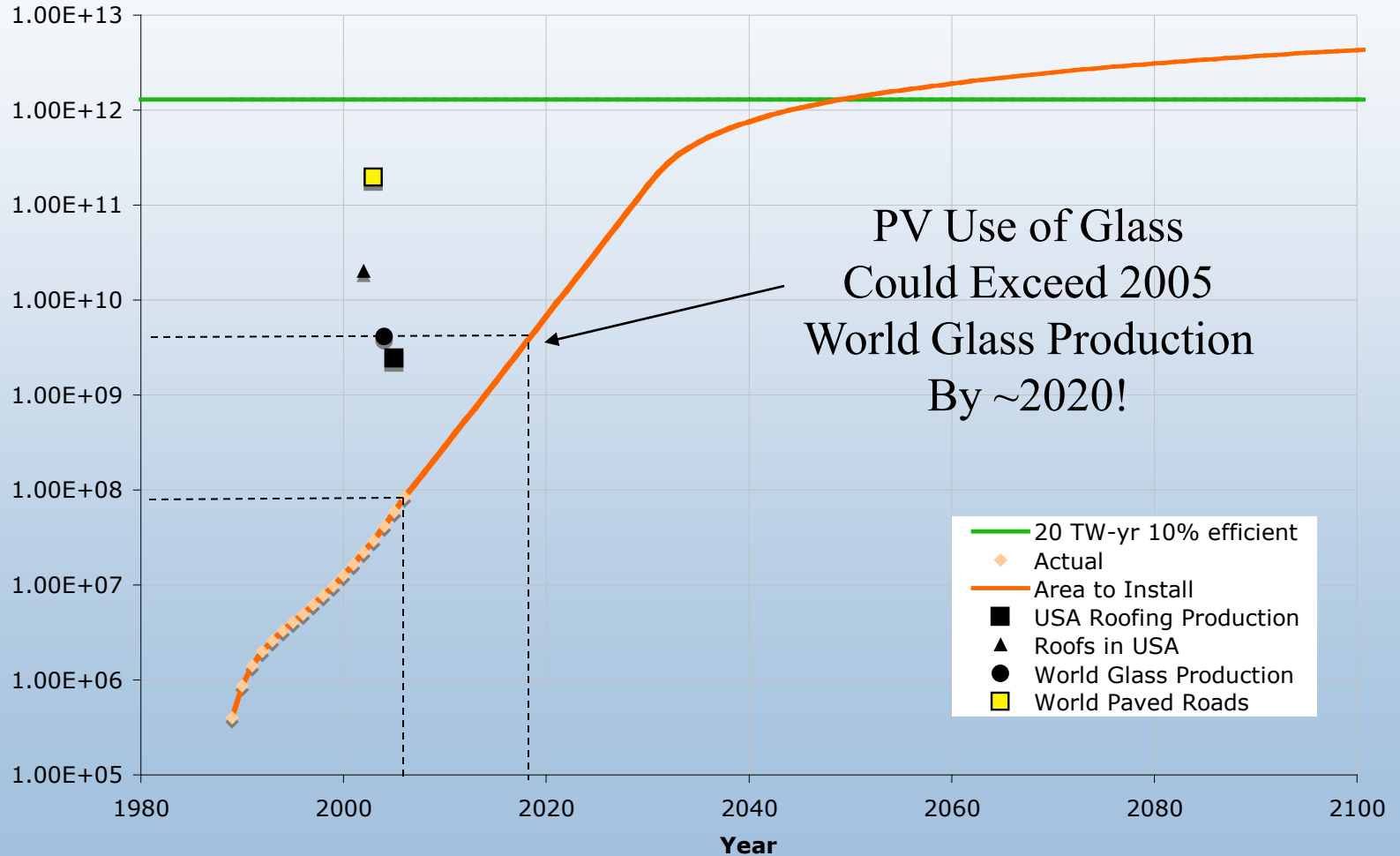
Sources: K. Zweibel, "PV Past the Tipping Point" ([www.nrel.gov/ncpv/thin\\_film](http://www.nrel.gov/ncpv/thin_film))  
PVWATTS Calculator, Version 1 ([http://rredc.nrel.gov/solar/codes\\_algs/PVWATTS/](http://rredc.nrel.gov/solar/codes_algs/PVWATTS/))

Note:  
Munich, Germany  
~1100 KWH/m<sup>2</sup>



# Example - Size of PV Market for Commercial Glass

Area of PV Installed



# Some CIGS-alloy, CdTe, & a-Si Laboratory Cell NREL-Confirmed Record Efficiencies

Material	Area (cm <sup>2</sup> )	V <sub>oc</sub> (V)	J <sub>sc</sub> (mA/cm <sup>2</sup> )	FF (%)	Efficiency (%)	Comments
CIGSe	0.410	0.697	35.1	79.52	20.0	CIGSe/CdS/Cell NREL, 3-stage process
CIGSe	0.402	0.67	35.1	78.78	18.5	CIGSe/ZnS (O,OH) NREL, Nakada et al
CIGS	0.409	0.83	20.9	69.13	12.0	Cu(In,Ga)S <sub>2</sub> /CdS Dhere, FSEC
CIAS	–	0.621	36.0	75.50	16.9	Cu(In,Al)Se <sub>2</sub> /CdS IEC, E <sub>g</sub> = 1.15eV
CdTe	1.03	0.845	25.9	75.51	16.7	CTO/ZTO/CdS/CdTe NREL, CSS
CdTe	–	0.814	23.56	73.25	14.0	ZnO/CdS/CdTe/Metal U. of Toledo, sputtered
a-Si	-	-	-	73.25	12.1	United Solar, Stabilized Efficiency

Sources: Updated from R. Noufi and K. Zweibel, Proc. 4th WCPEC, Waikola, Hawaii, 5/2006, Photon International, October 2004

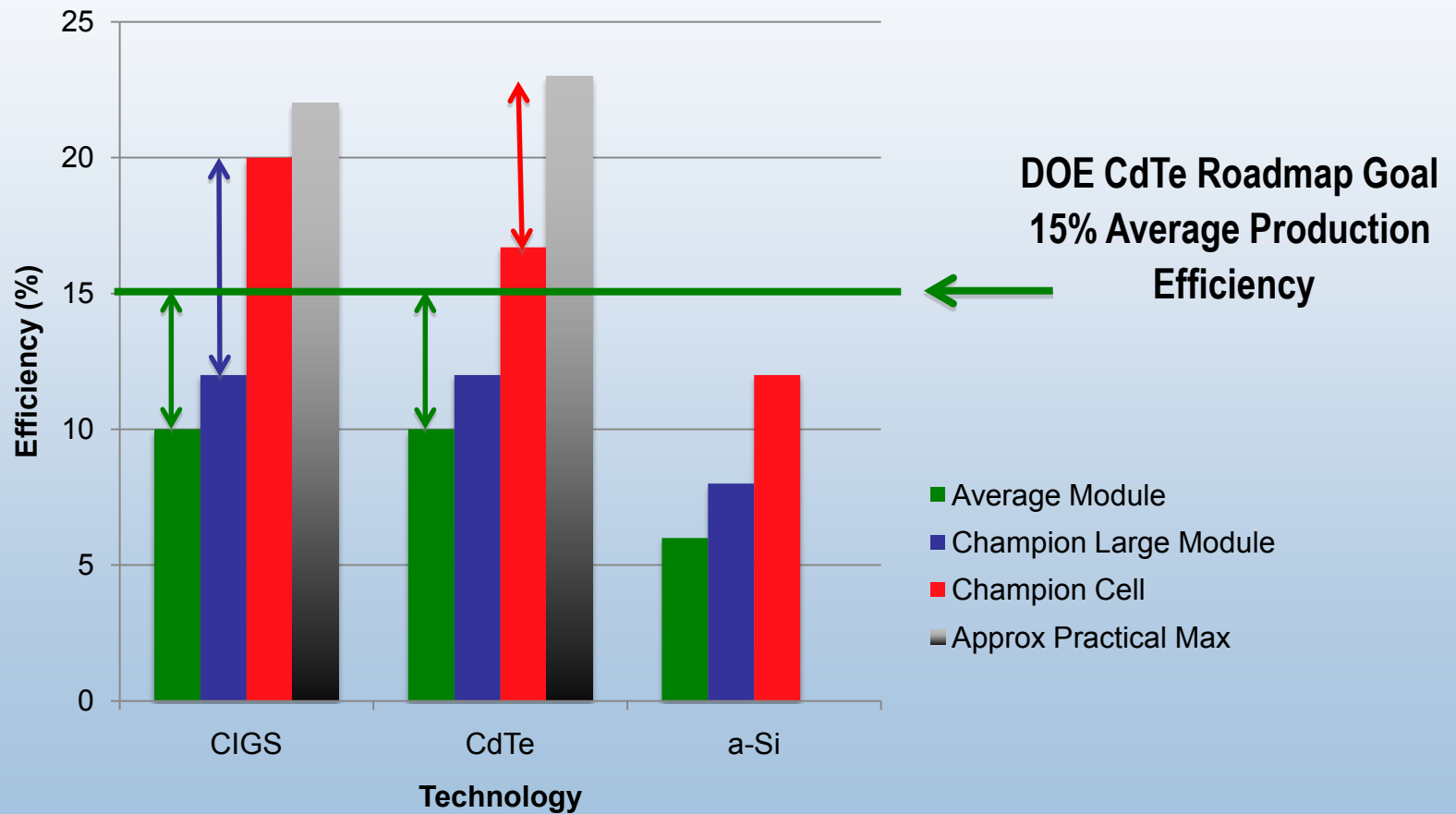
# Polycrystalline Thin Film PV Modules (Standard conditions, Aperture-area, \*NREL Confirmed) Ranked by Power

Company	Device	Aperture (cm <sup>2</sup> )	Efficiency*(%)	Power (W)	Date
Miasole	CIGS	9762	13.6-13.8	-	4/10
Global Solar	CIGS	8390	10.2*	88.9	8/02
<b>First Solar</b>	<b>CdTe</b>	<b>6623</b>	<b>12.6*</b>	<b>84.4</b>	<b>8/08</b>
Wurth Solar	CIGS	6500	13.0	84.6	6/04
<b>United Solar</b>	<b>a-Si</b>	<b>4519</b>	<b>7.9*</b>	<b>35.7</b>	<b>6/97</b>
Shell Solar	CIGSS	3626	12.8*	46.5	3/03
Showa Shell	CIGS	3459	13.5	-	8/02

Sources: Updated From R. Noufi and K. Zweibel, Proc. 4th WCPEC, Waikola, Hawaii, 5/2006, Photon International October 2004,

# Goal

## Increase Average Production Module Efficiency



# Present Strengths of Each Thin-film PV Technology

	Demonstrated Efficiency	Perceived Production Advantage	Perceived Materials Abundance/ Low Toxicity
a-Si			Strength
CdTe		Strength	
CIS	Strength		

Thoughts:

Each technology has different advantages

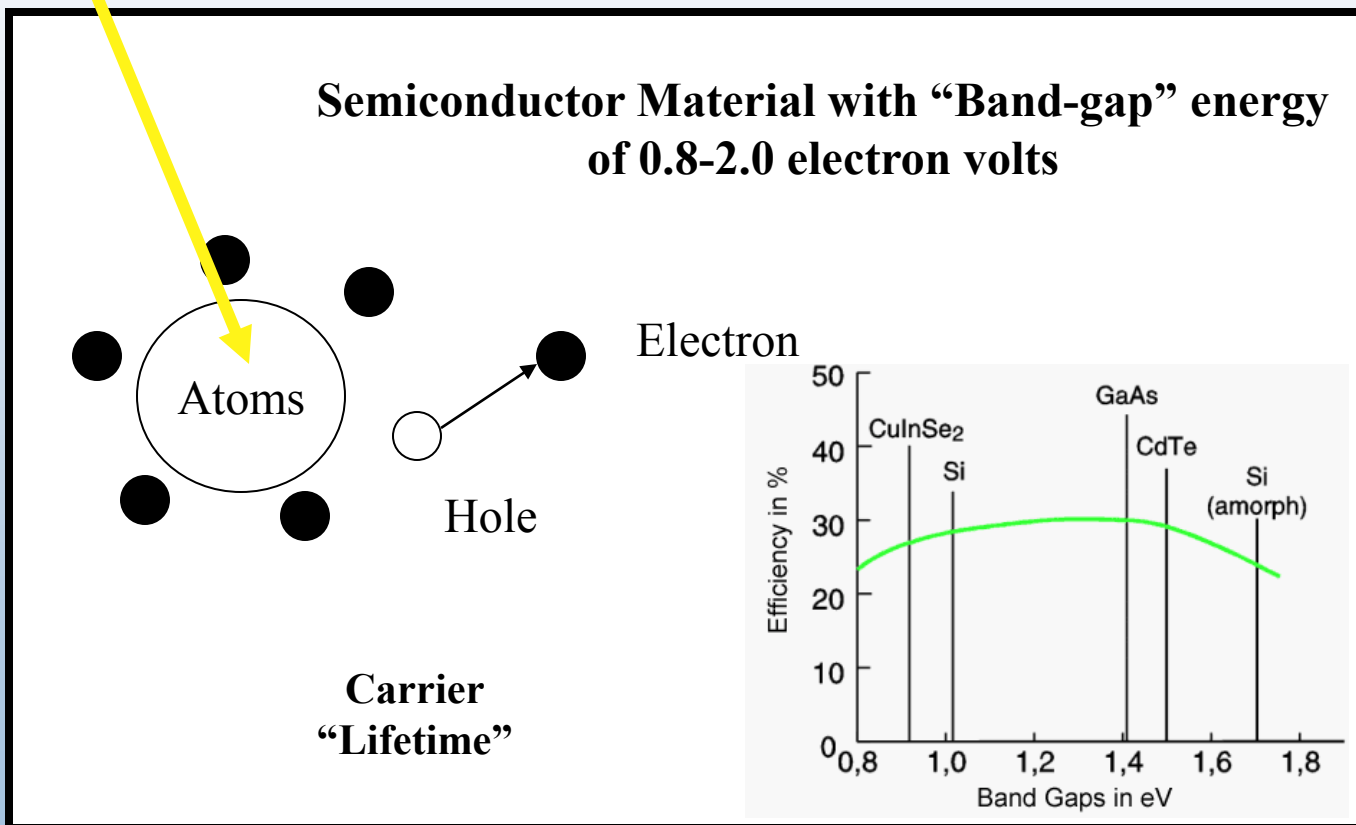
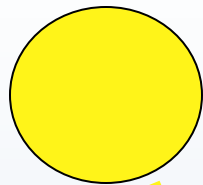
Its not clear which (if any) advantage will yield a long-term product advantage

This situation could remain true for many years!

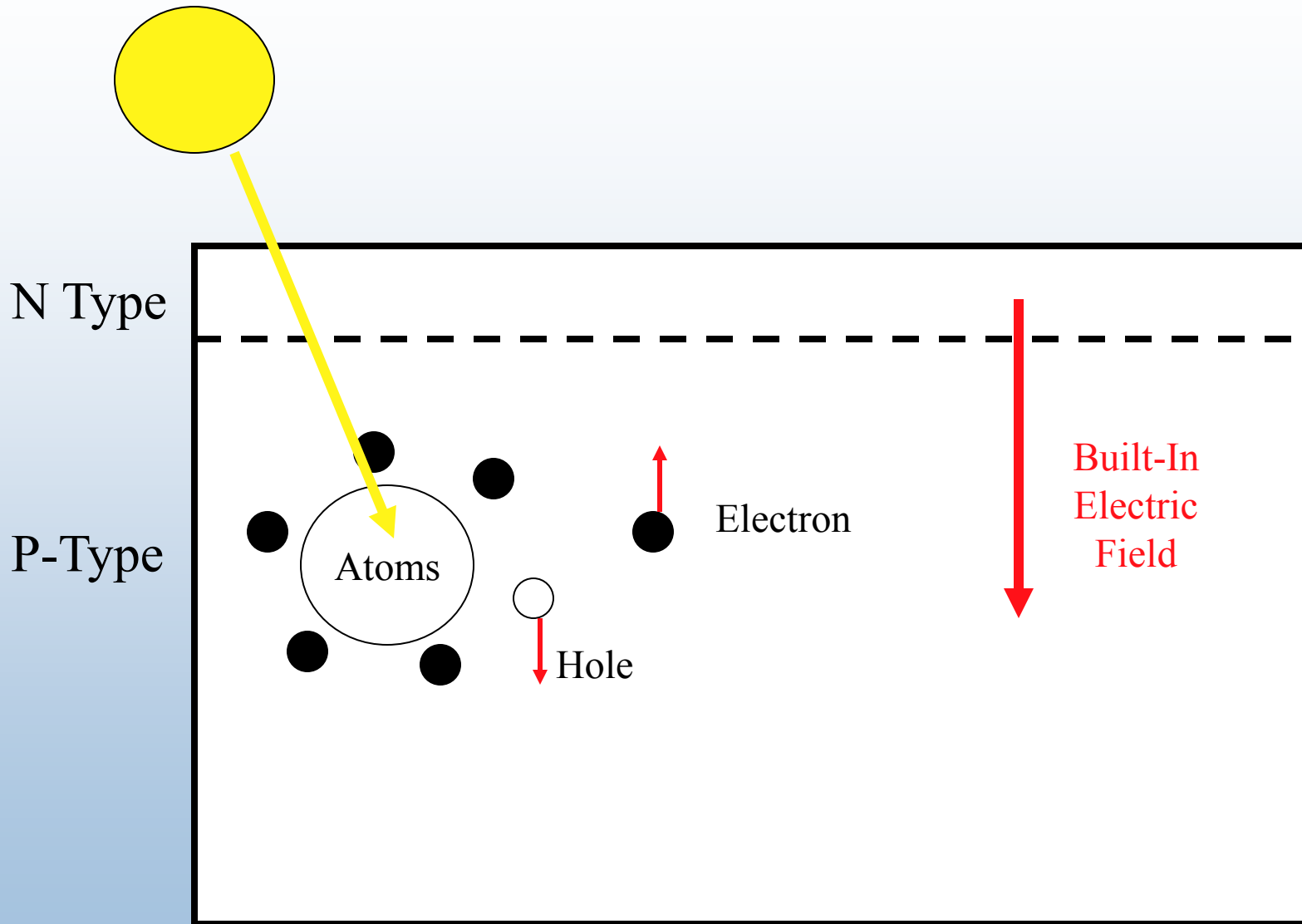


# How Do These Things Work?

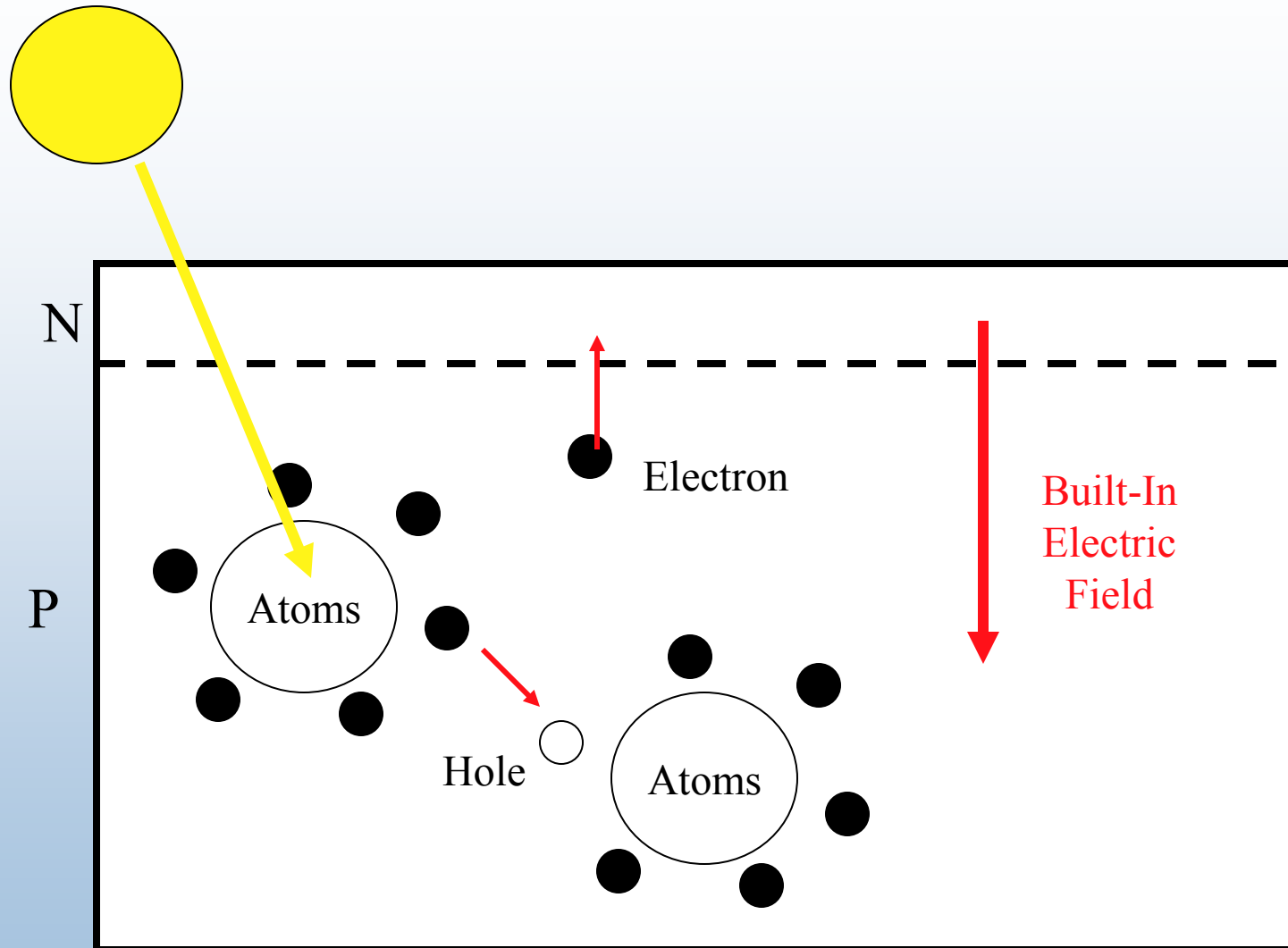
## PV Device Operation 101



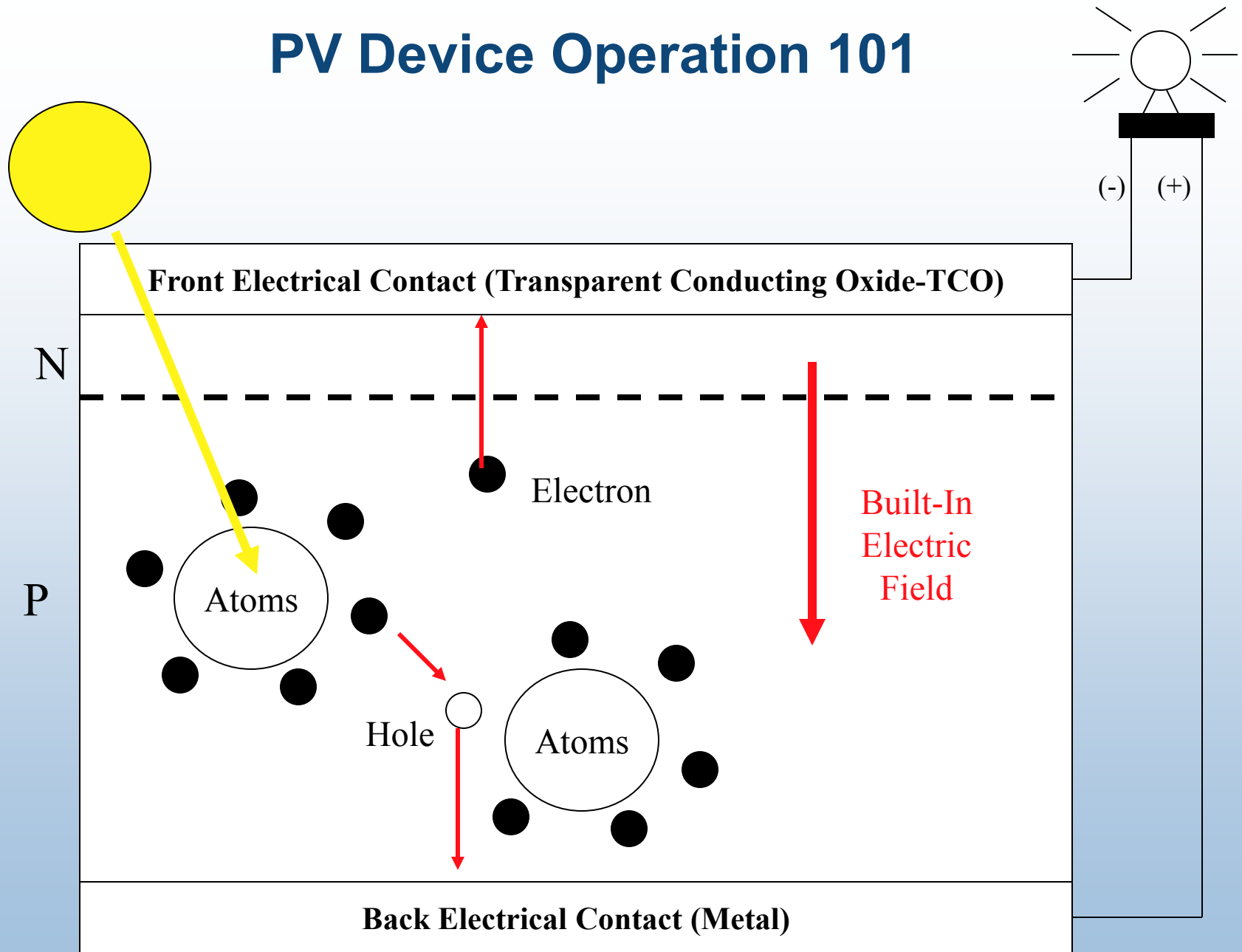
# PV Device Operation 101



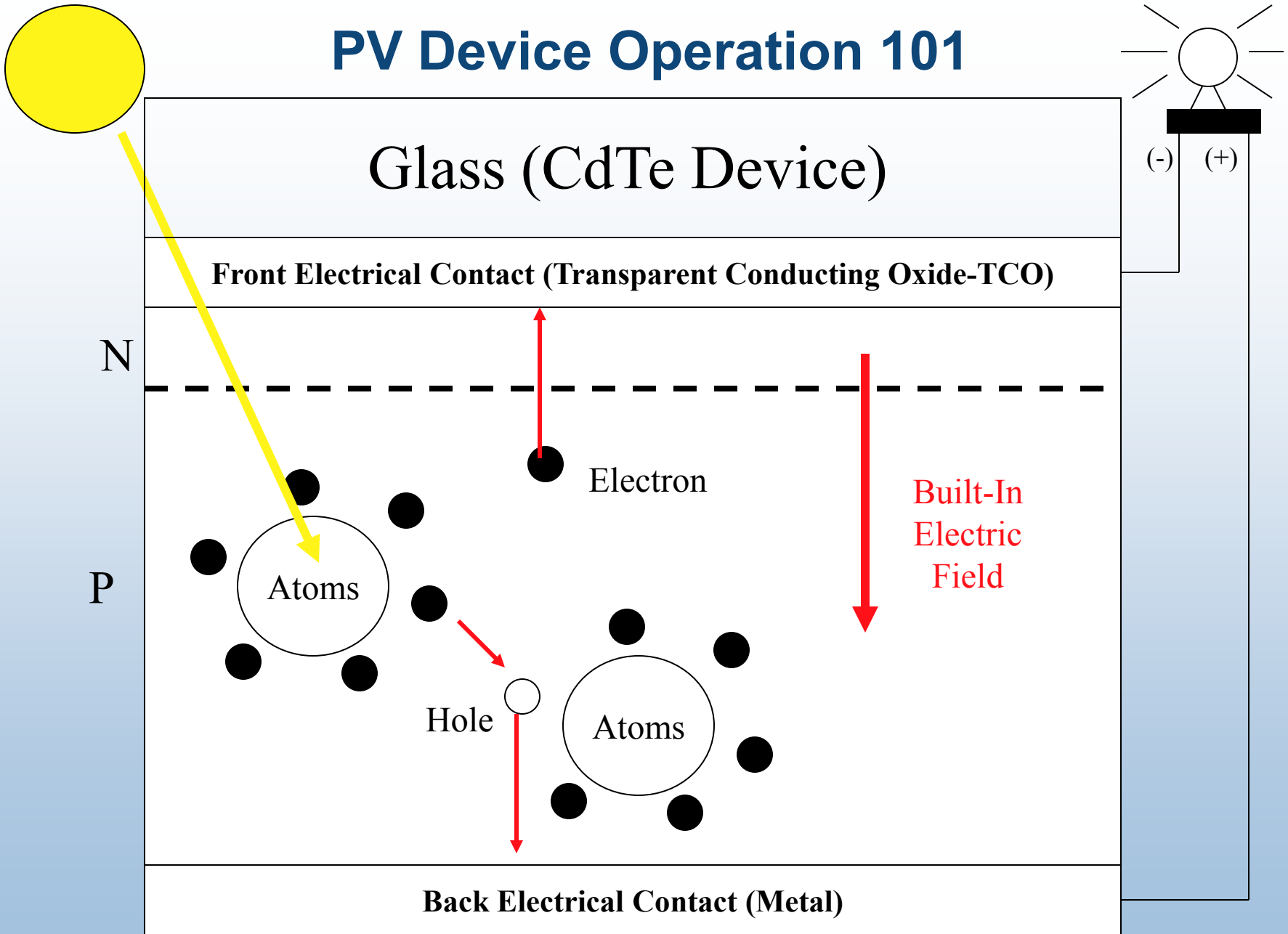
# PV Device Operation 101



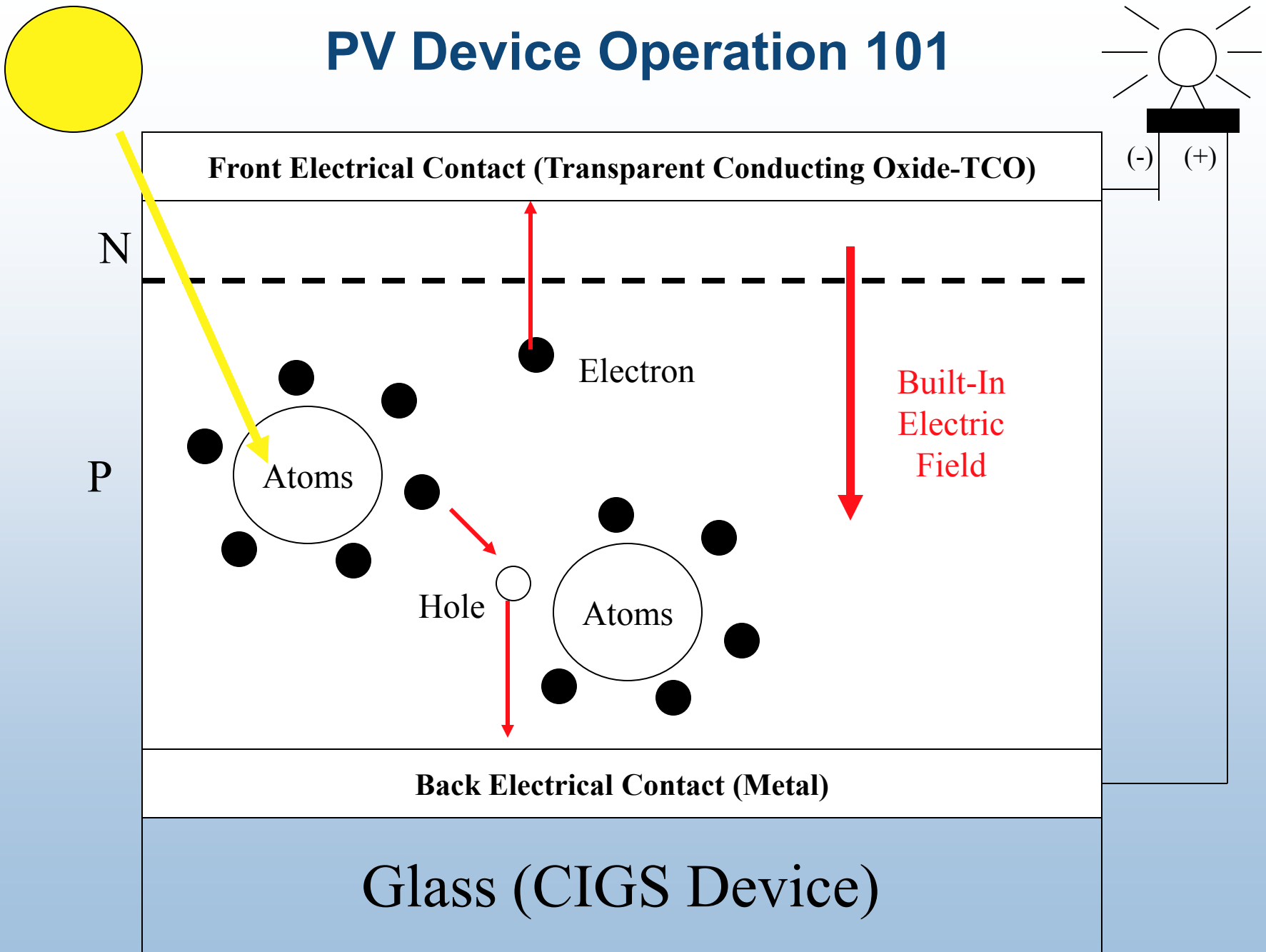
# PV Device Operation 101



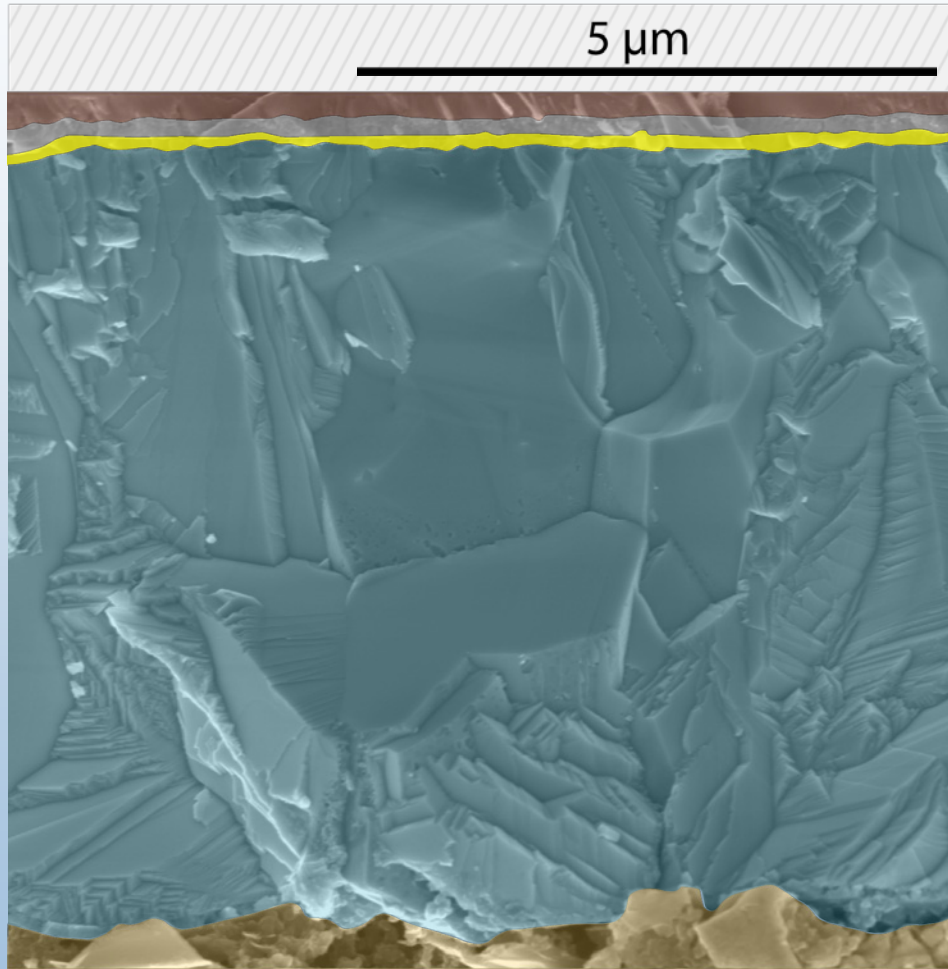
# PV Device Operation 101



# PV Device Operation 101



# Thin Film CdTe Solar Cells



Glass

TCO

CdS (600-2000 Å)

**CdTe**

2-8 μm

Cu-Containing  
Interface

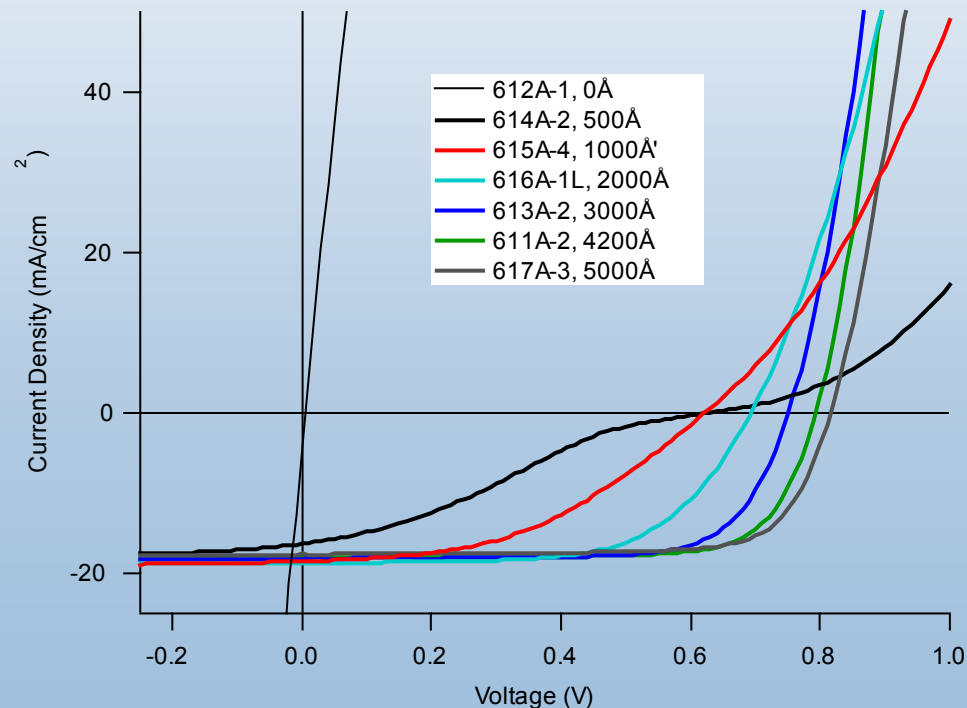
(Paste, Pretreatments,  
ZnTe:Cu) + Metals

$\eta = 16.7\%$   
(NREL)

# How do CdTe Thin-Film PV Junctions Form??

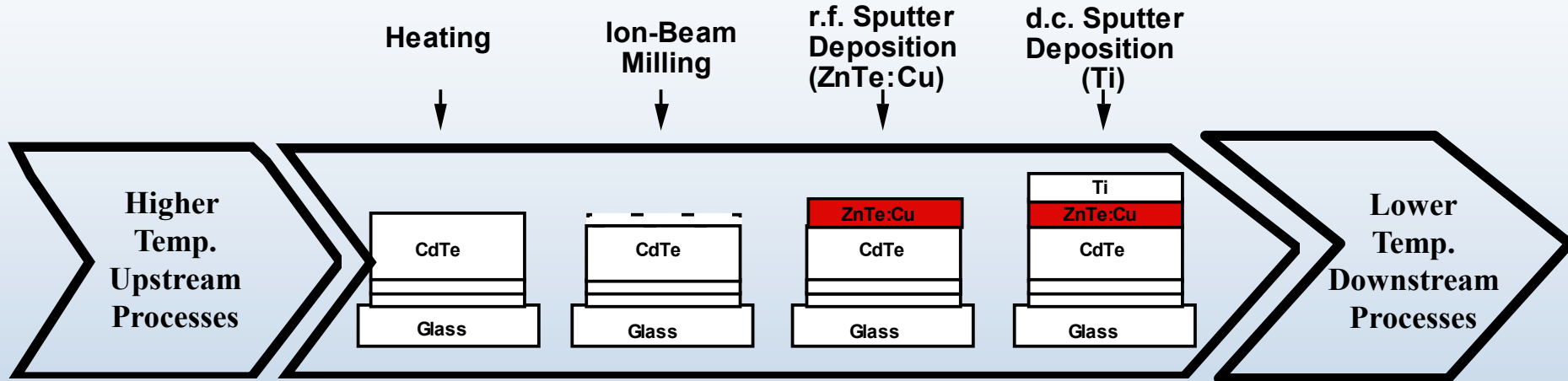
## What this really means:

How do we get the electric field to form in the device at the correct location and strength -  
- without destroying the minority-carrier lifetime?

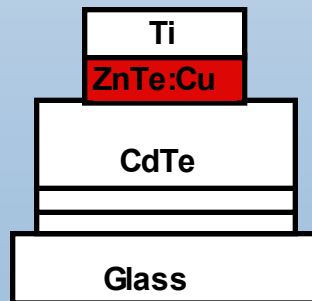




The ZnTe:Cu/Ti Contact Process  
(All-Dry, High-Temperature [ $\sim 300^{\circ}\text{C}$ ])



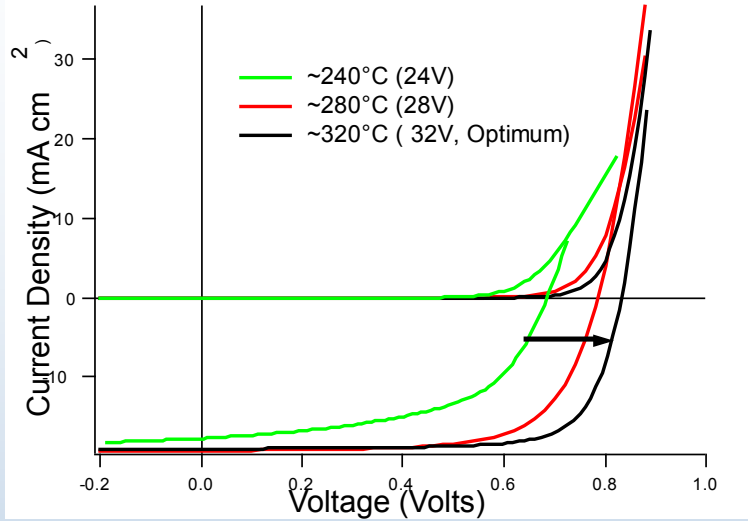
**Photolithography**



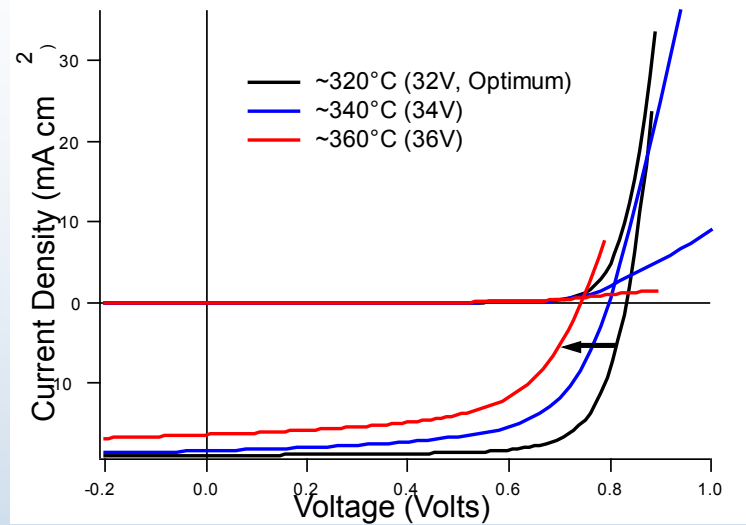
Some Research Advantages

- Precise control of junction performance
- High device stability
- Can achieve very low Cu incorporation
- Easy to make large, identical sample sets

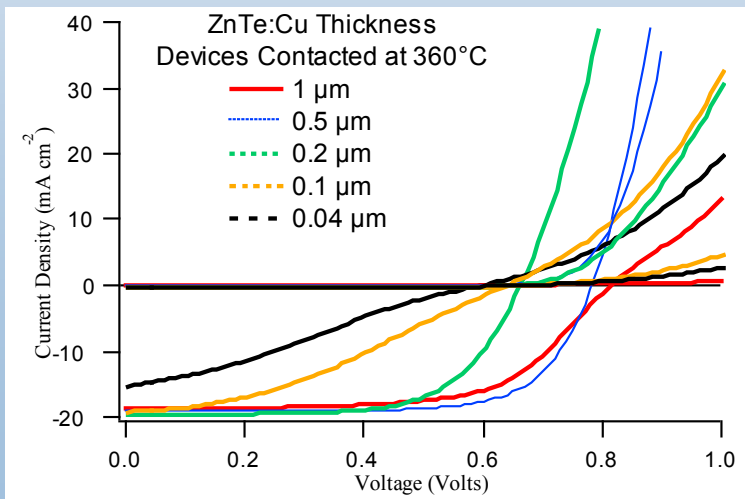
## Cu Diffusion Less Than Optimum



## Cu Diffusion Greater Than Optimum



Effect of Contacting Temperature

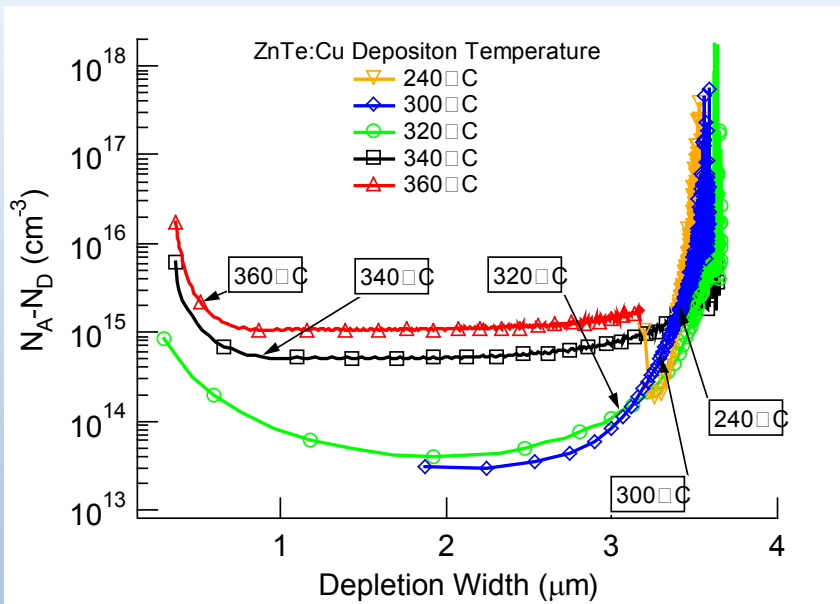


Effect of ZnTe:Cu Thickness

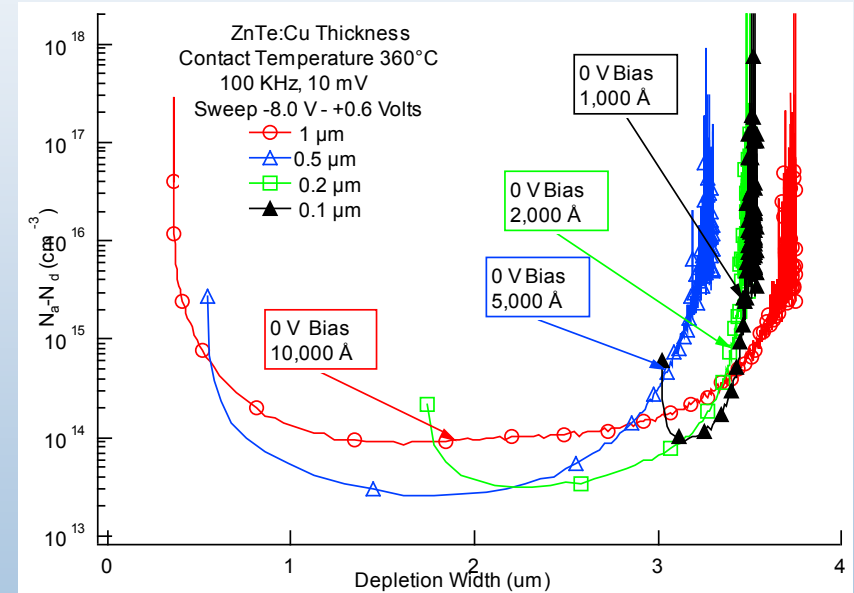


## Comparison of Profiling C-V Analysis

### Vary Contact Temperature

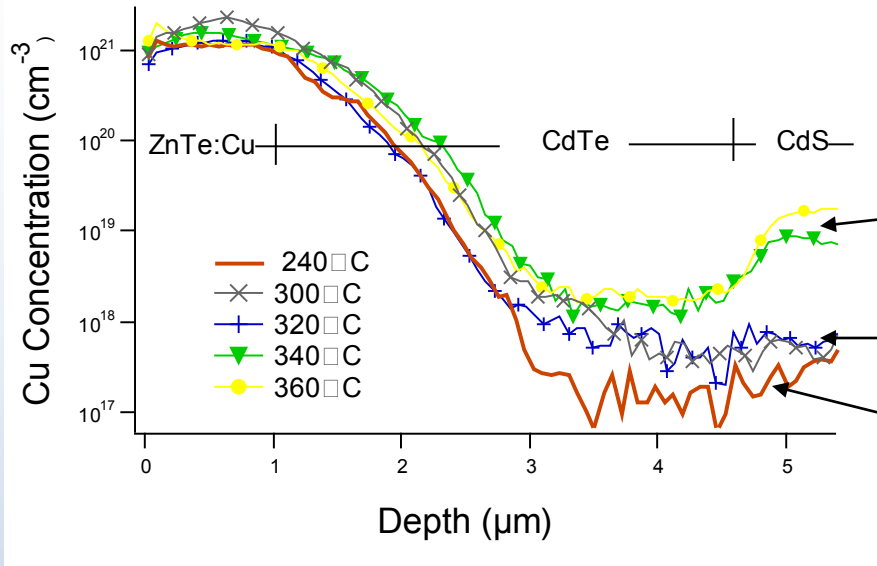


### Vary ZnTe:Cu Thickness



(100 kHz, 10 mV, -8.0 to +0.6 Sweep)





Vary Contact Temperature

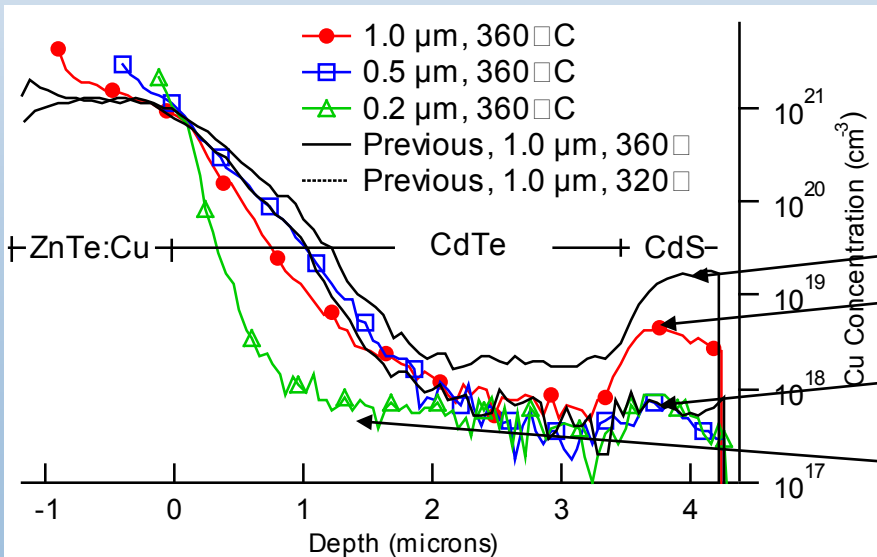
Excessive Cu

Optimum Cu

Insufficient Cu

**High-Resolution  
Compositional  
Depth-Profiling  
Secondary Ion**

**Mass Spectrometry  
Analysis  
(SIMS)**



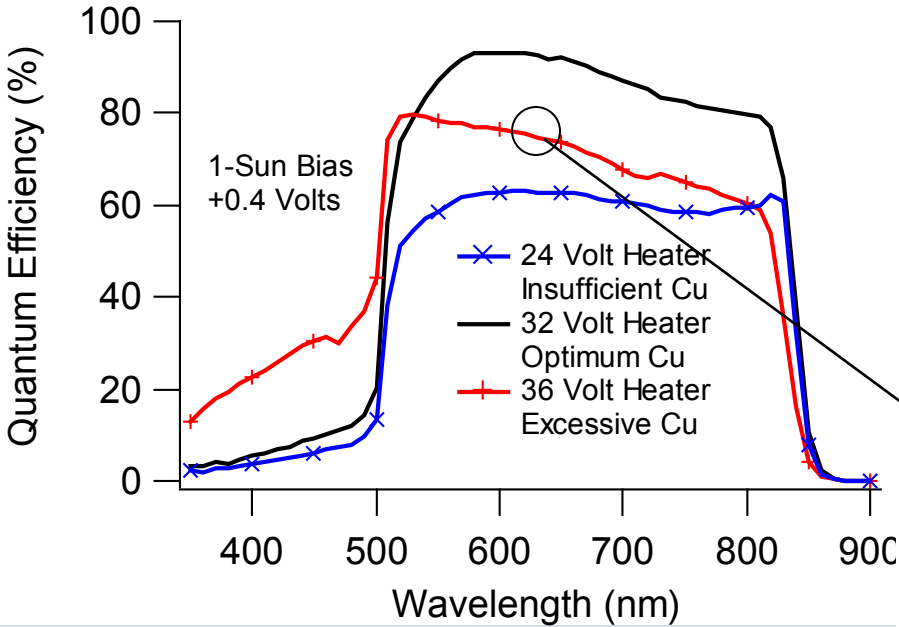
Vary Contact Thickness

Excessive Cu

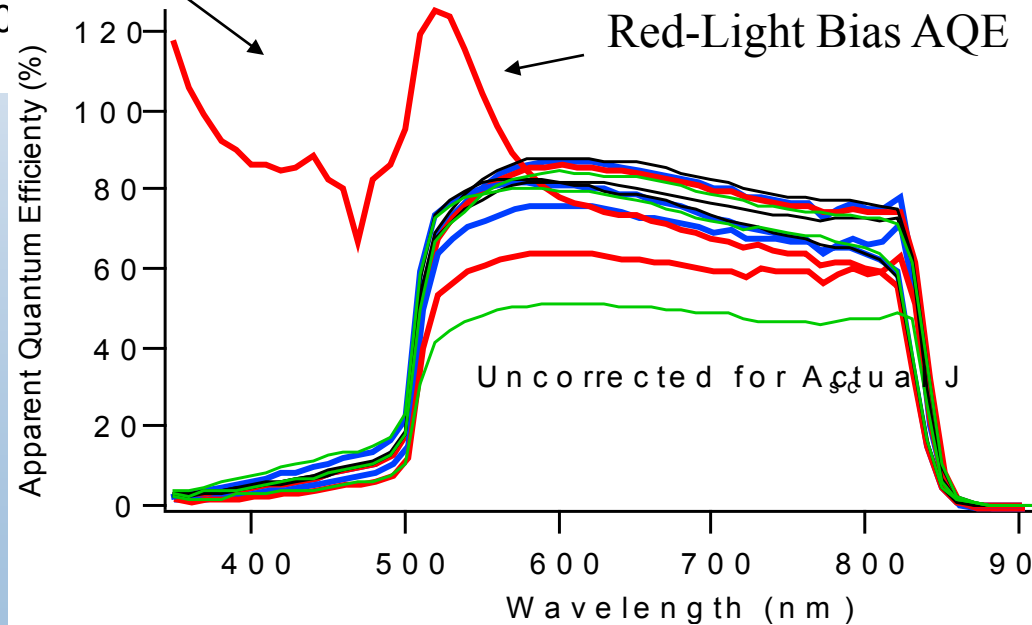
??

Optimum Cu

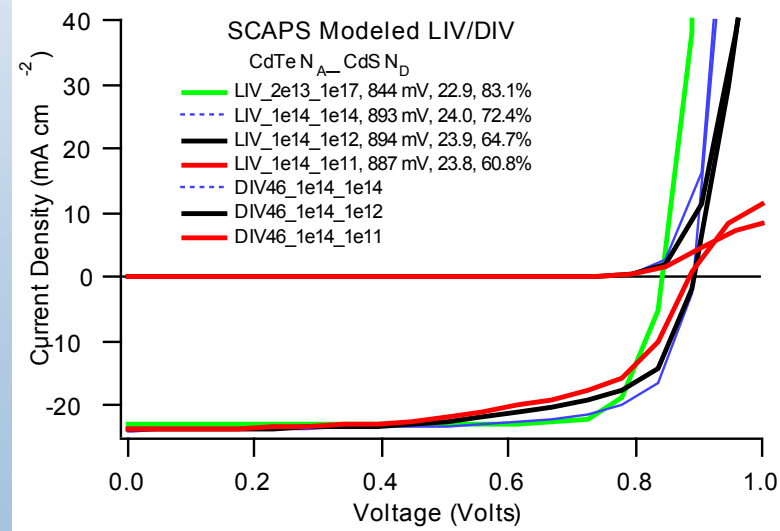
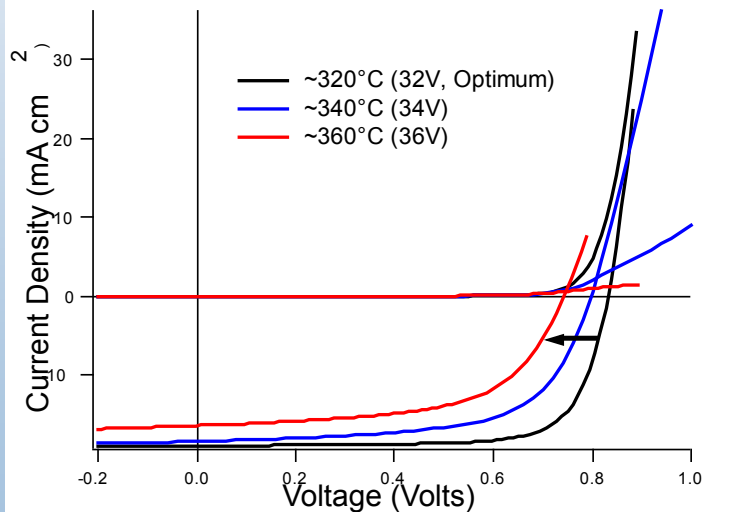
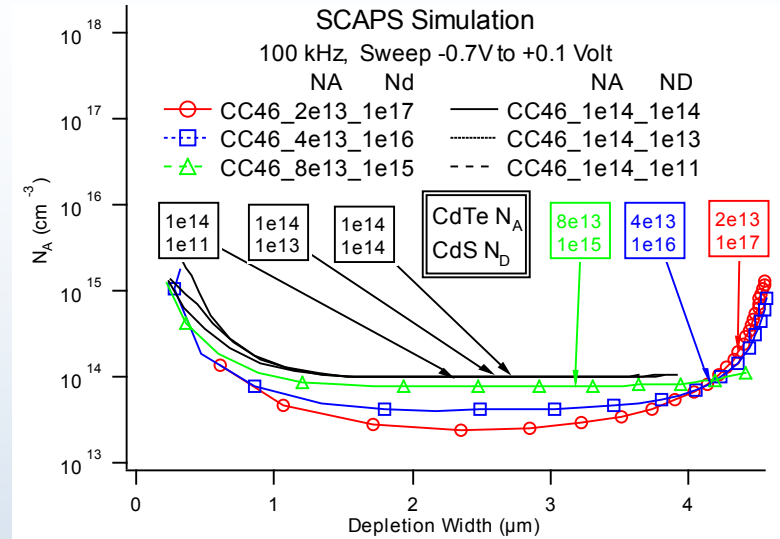
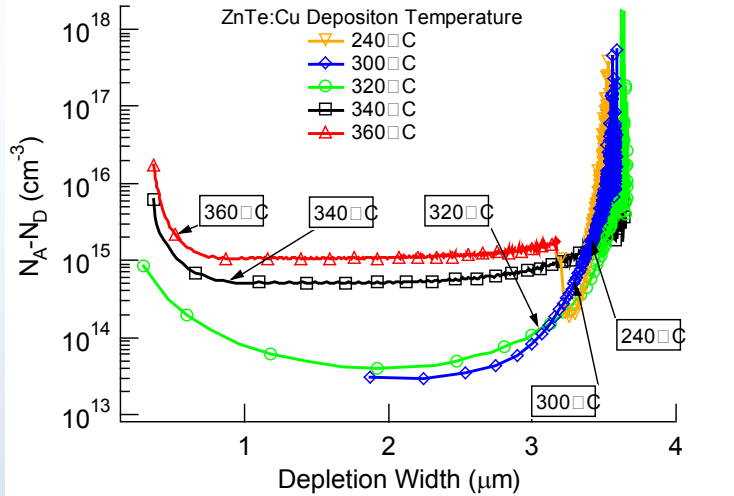
Insufficient Cu



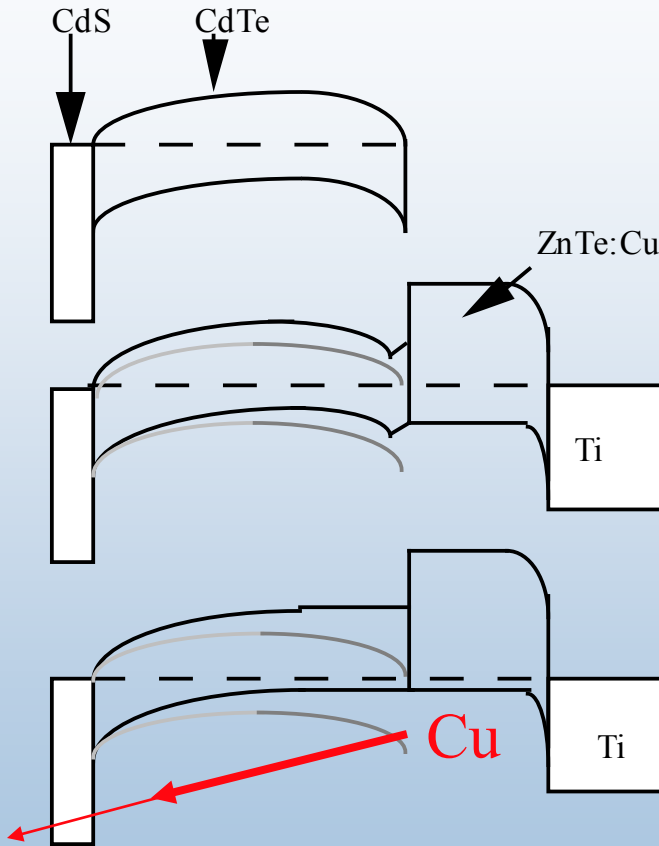
Red-Light Bias QE Confirms  
Photoconductive CdS  
Only For “Excessive” Cu Devices



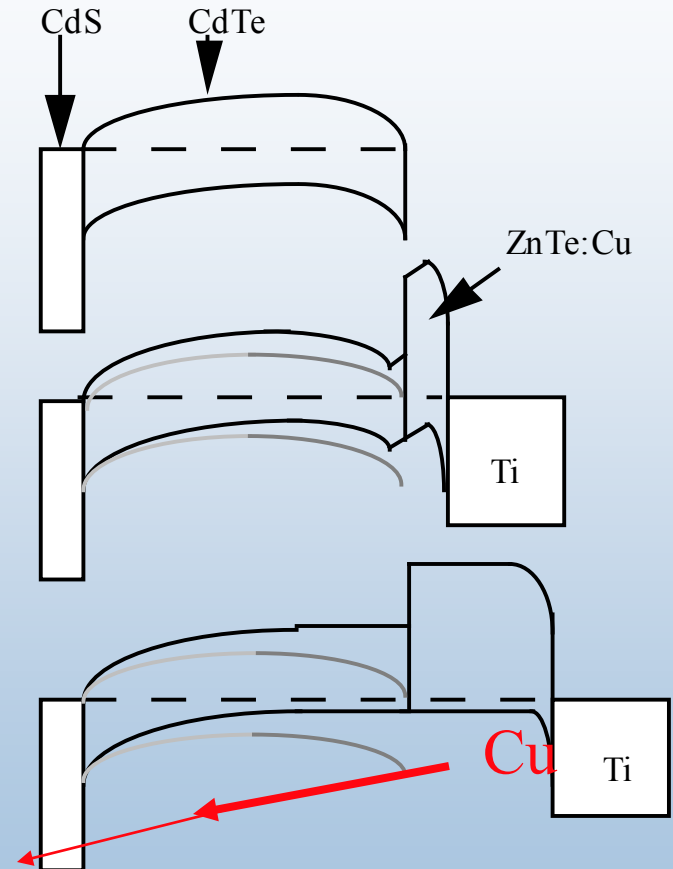
QE Comparison Suggests  
Narrowing Junction  
for Excessive Cu Devices



**Constant Thickness  $\sim 0.5 \mu\text{m}$**   
**Vary ZnTe:Cu Temperature**

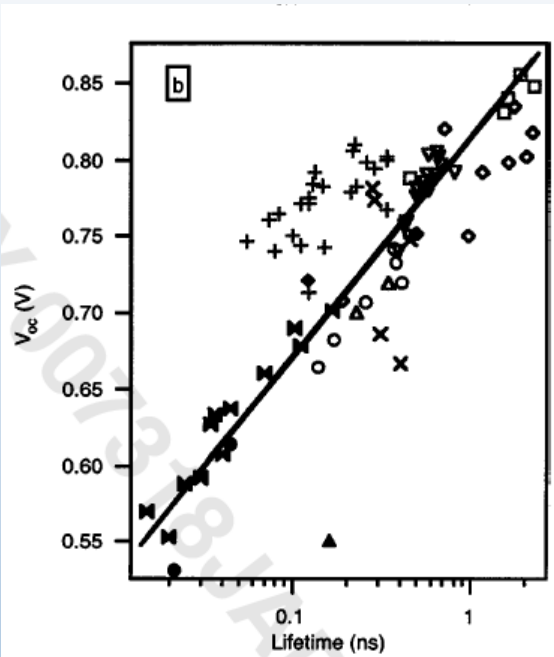


**Constant Temperature  $\sim 300^\circ\text{C}$**   
**Vary ZnTe:Cu Thickness**

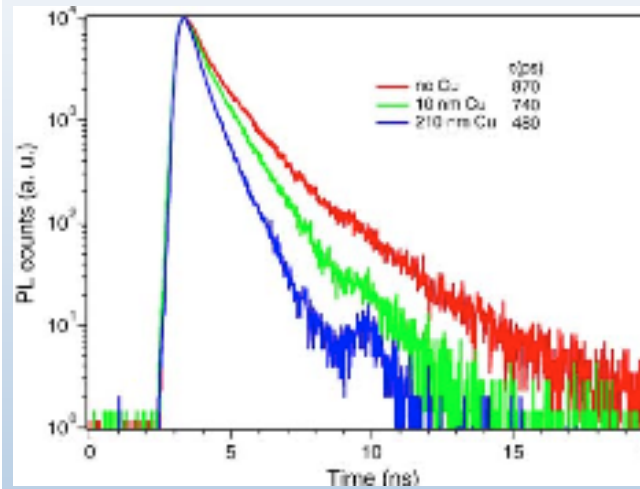


But...Assumes Minority Carrier Lifetime Does Not Change

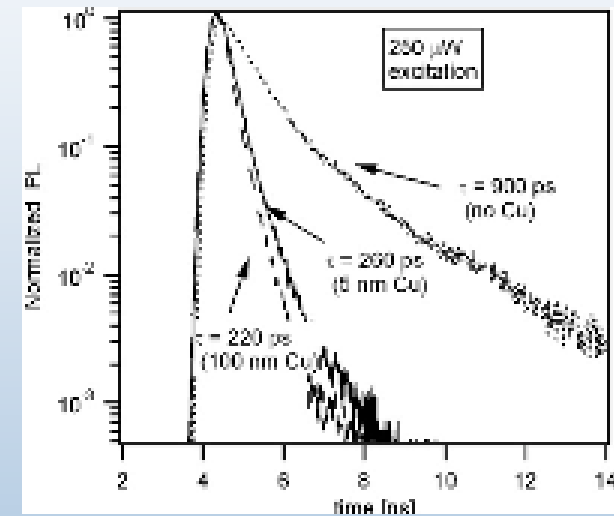
## Previous TRPL studies indicate minority carrier lifetime decreases with Cu



Metzger, Albin, Levi, Sheldon, Li, Keyes, Ahrenkeil, JAP 94(6) (2003)



Wu, Zhou, Duda, Yan, Teeter, Asher, Metzger, Demtsu, Wei, Noufi, TSF, 515, 5798 (2007)

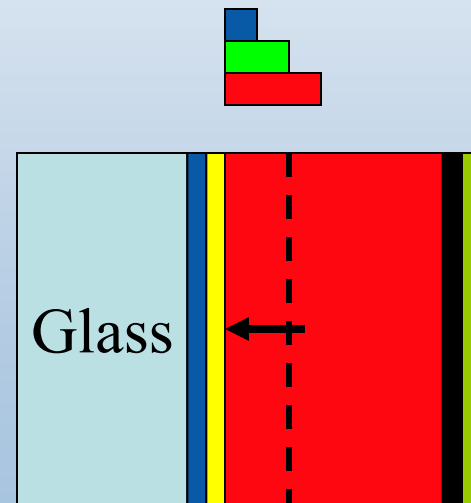
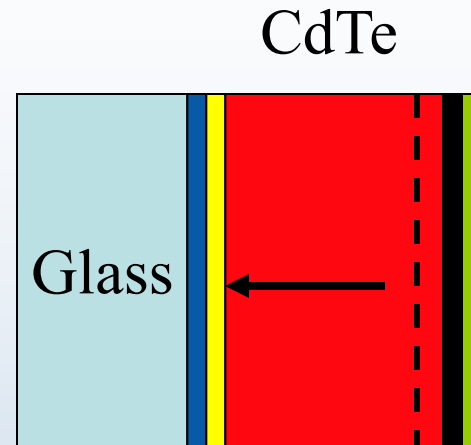
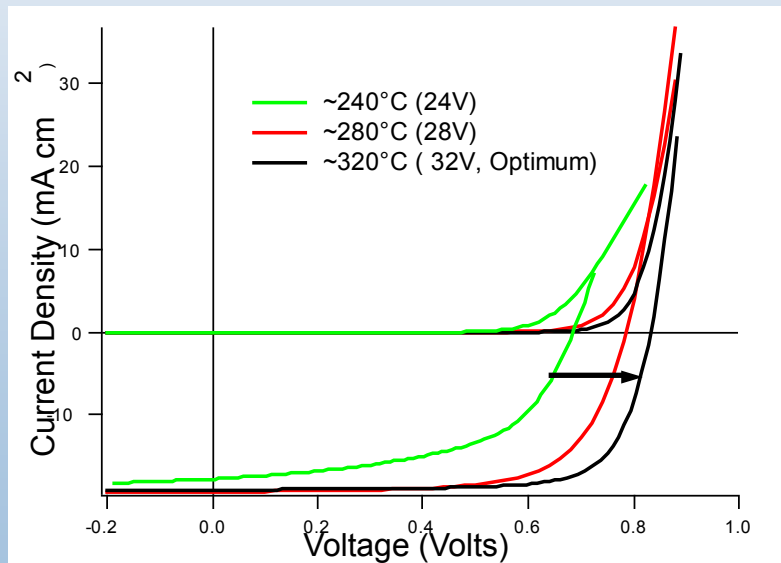


Demtsu, Albin, Sites, Metzger, Duda, TSF, 516 p. 2251 (2008)

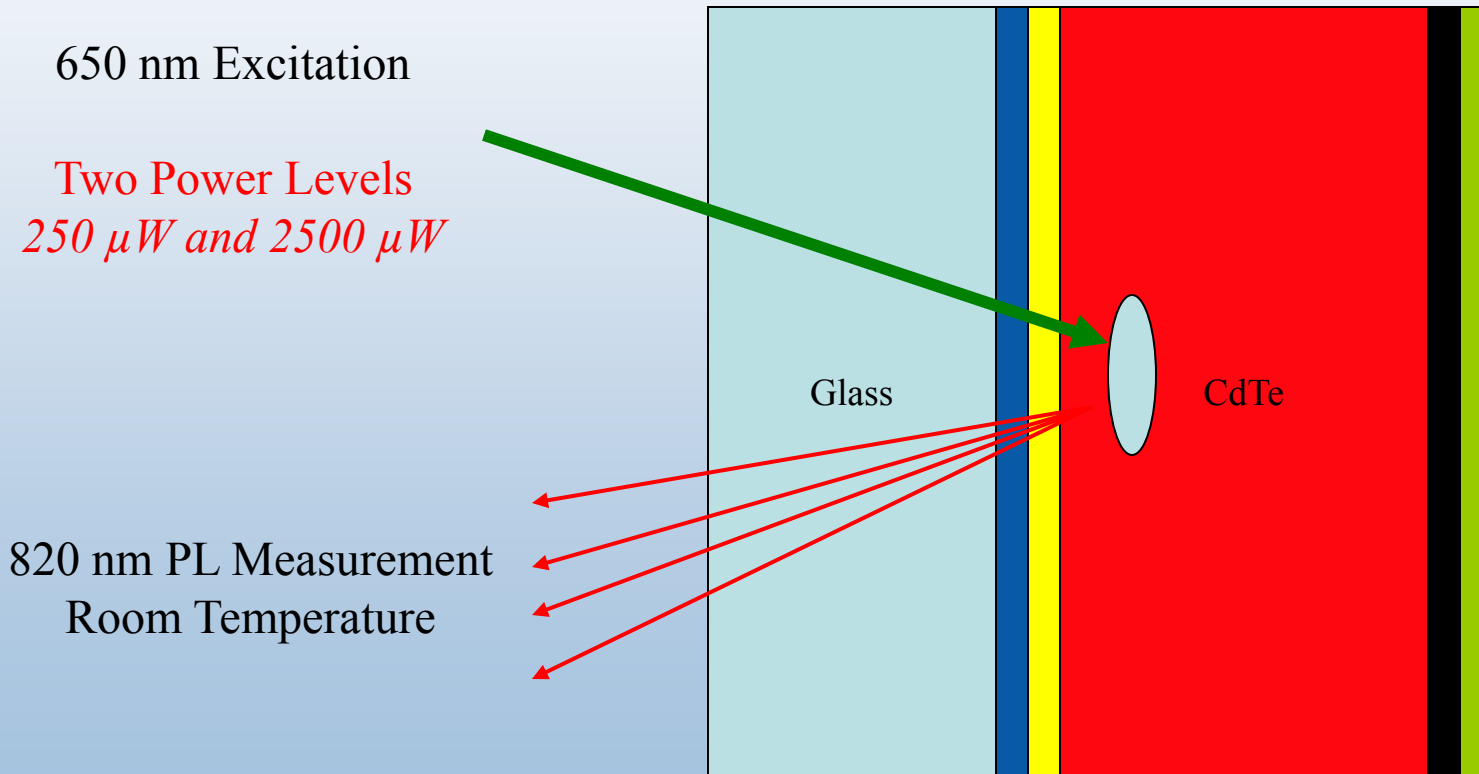


## Question

If both carrier lifetime and space charge width decreases with Cu incorporation, why does voltage-dependant collection decrease?

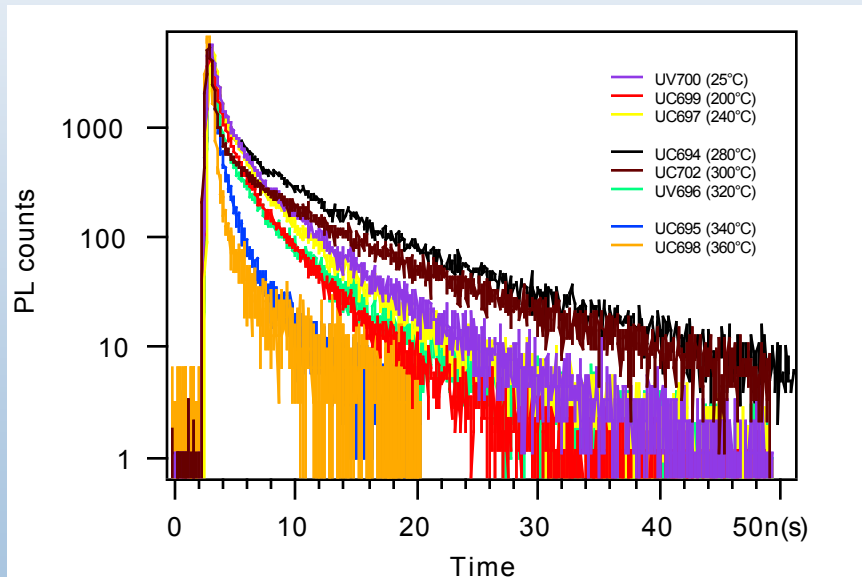


# Time Resolved Photoluminescence (TRPL)

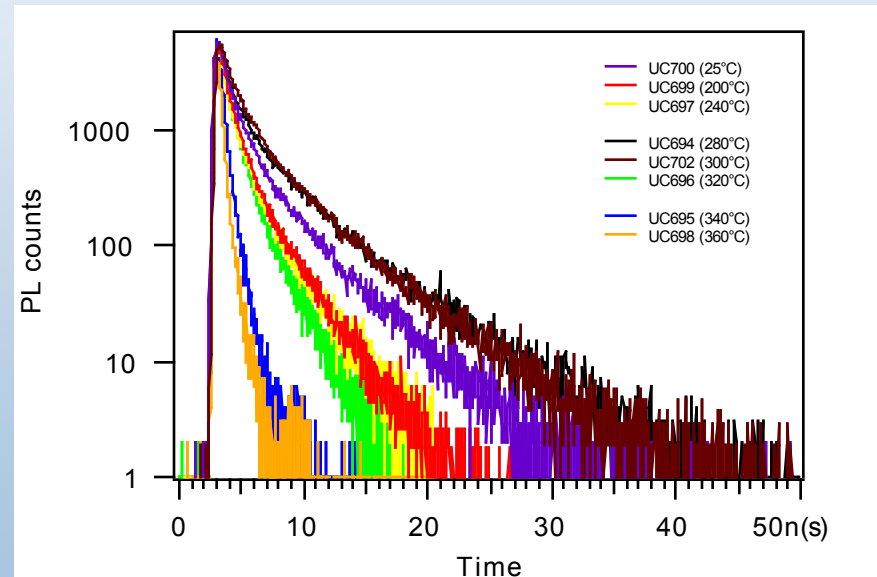


## TRPL Study of Cu Diffusion and Contact Temperature

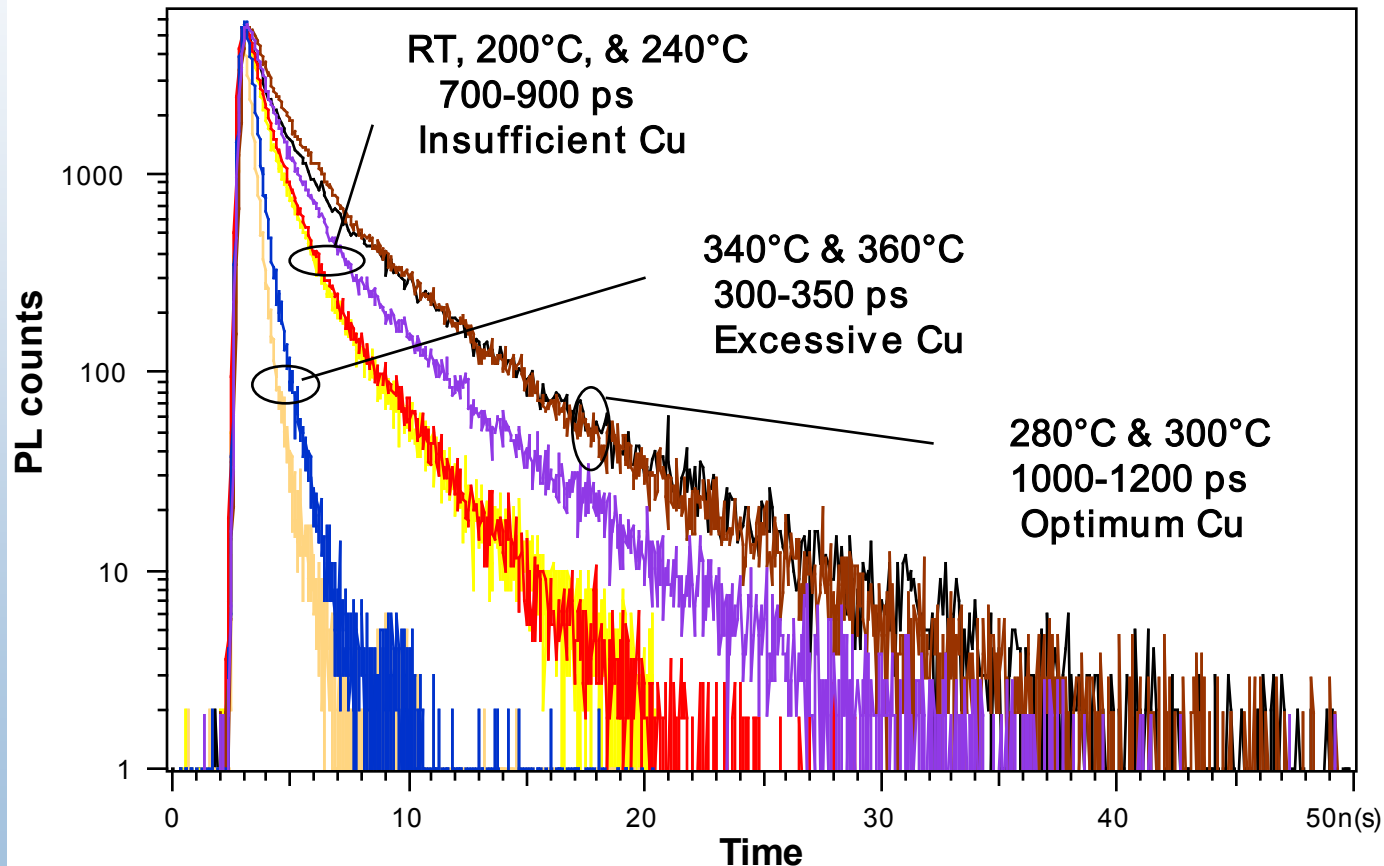
250  $\mu\text{W}$  Power



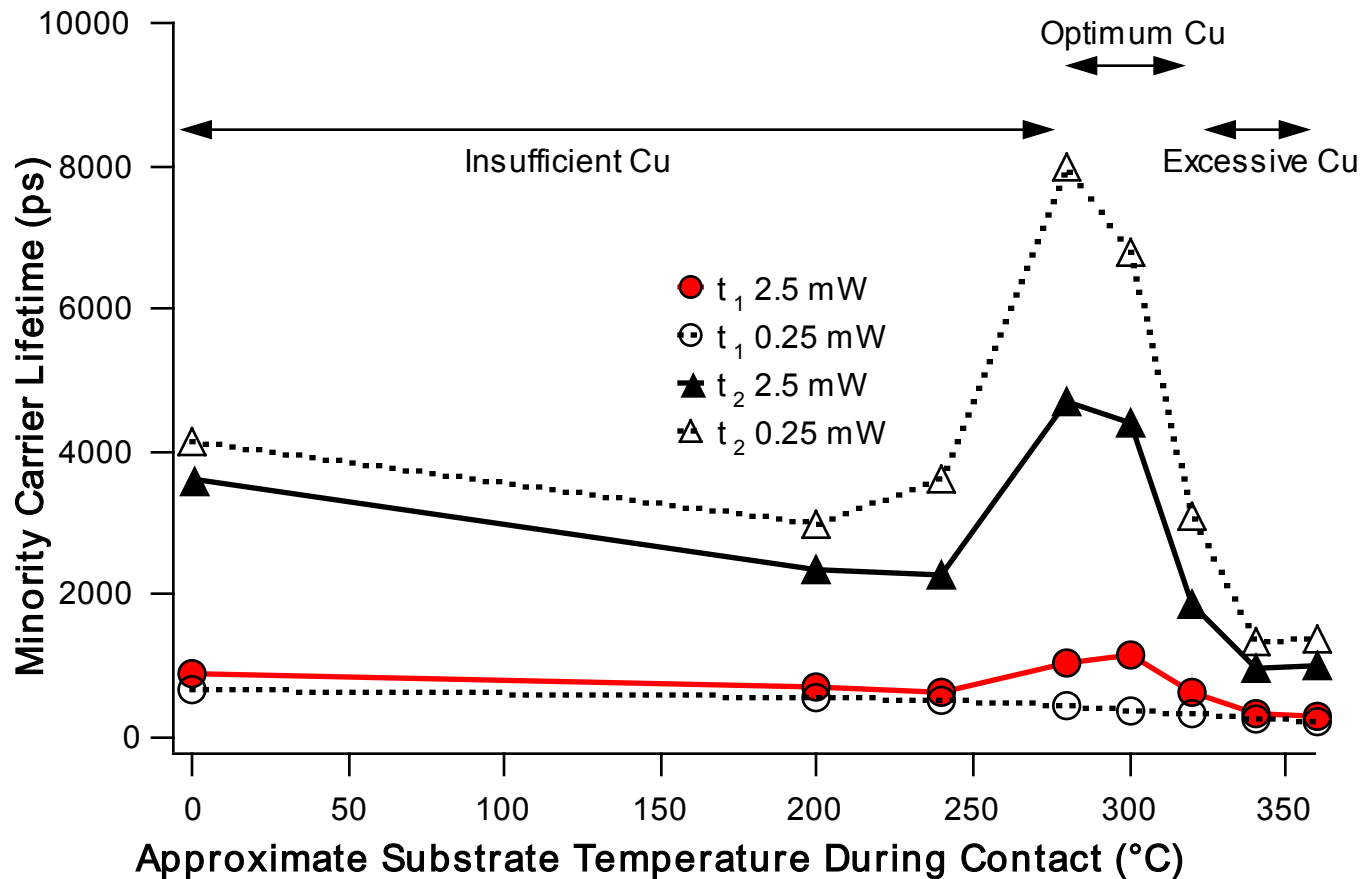
2500  $\mu\text{W}$  Power



# TRPL Study of Cu Diffusion and Contact Temperature (2500 $\mu$ W Power)



# Time Resolved Photoluminescence (TRPL)

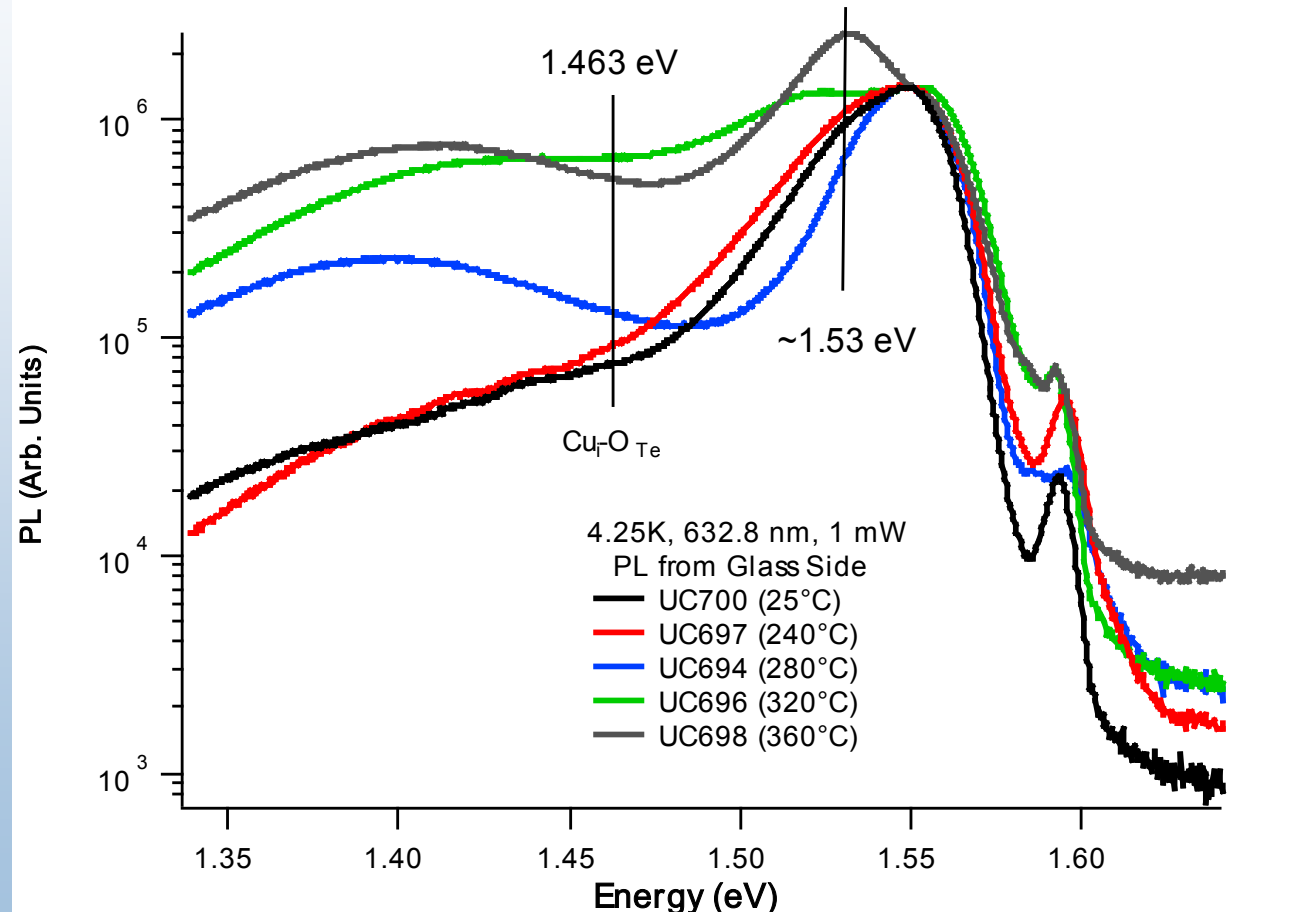


# Low-Temperature Photoluminescence (LTPL)

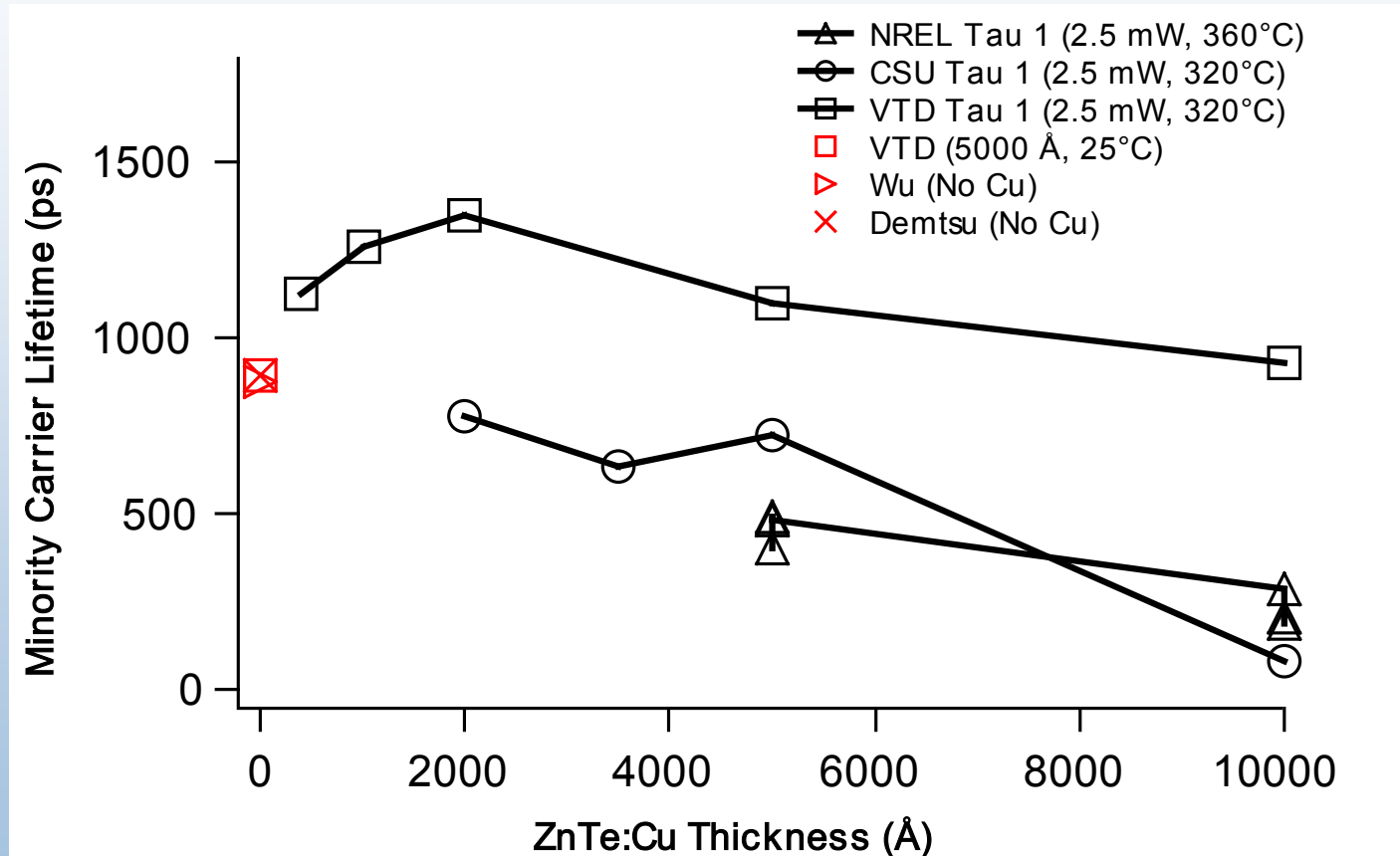
Increasing Contact Temperature produces peak that has been associated with a defect complex  $\text{Cu}_i\text{-O}_{\text{Te}}$ , and an unidentified peak at  $\sim 1.53$  eV

## Reference for $\text{Cu}_i\text{-O}_{\text{Te}}$

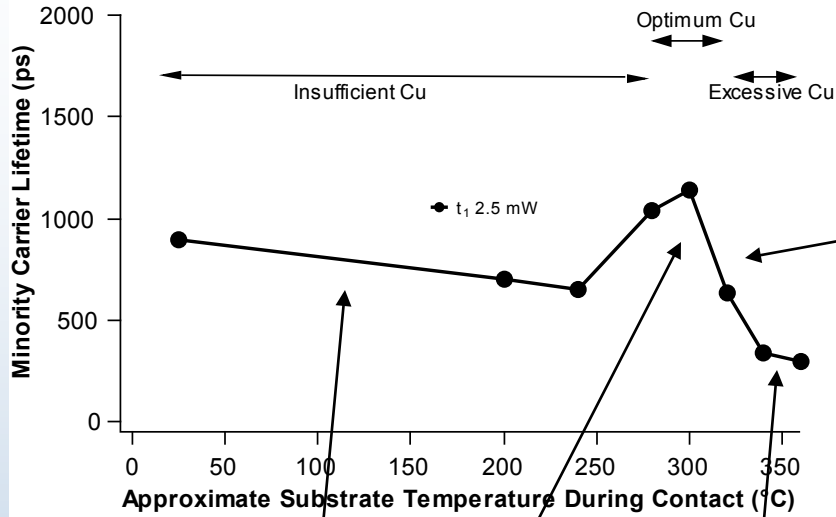
Corwine, Sites, Gessert, Metzger, and Duda, Appl. Phys Lett. 86 (1) 221909 (2005)



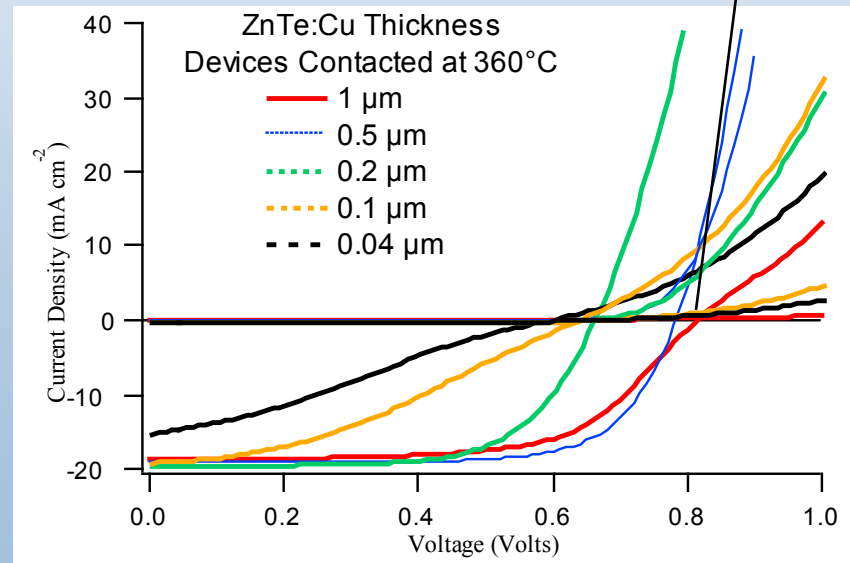
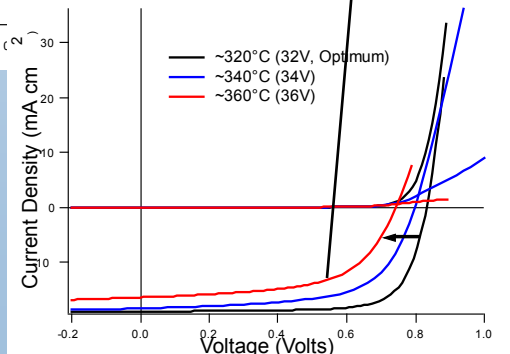
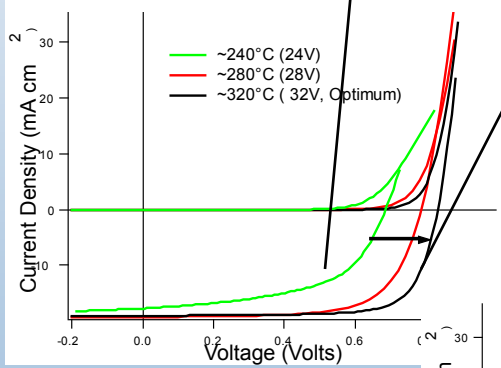
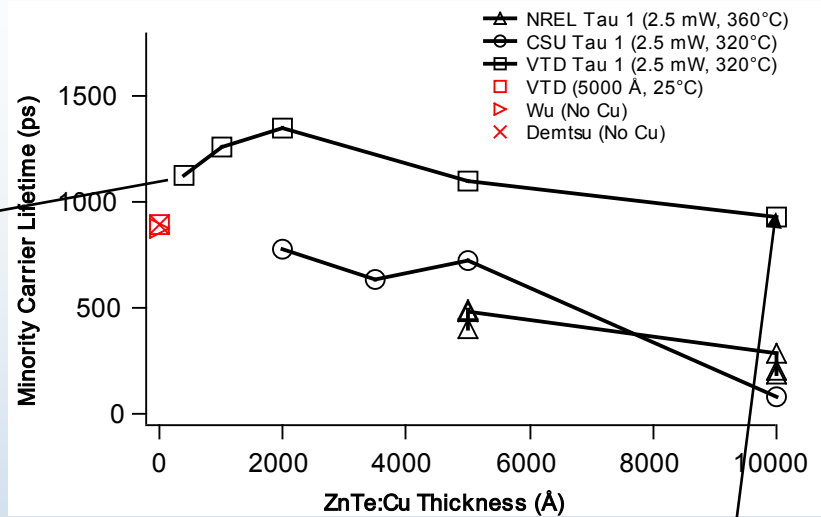
# Time Resolved Photoluminescence (TRPL)



## Constant Cu, Vary Temp



## Constant Temp, Vary Cu





## CdTe PV Devices Conclusions

- Net acceptor level increases during contacting, control produces optimum  $W_{\text{depletion}}$
- Minority carrier lifetime can decrease and/or increase during contacting
  - Primarily depends on temperature during Cu diffusion
  - Also depends on amount of Cu diffused
  - Reason(s) remain uncertain
- For the ZnTe:Cu/Ti contact, the longest lifetimes occur at contact temperature of  $\sim 280\text{-}320^{\circ}\text{C}$ 
  - This may explain various contact-process functionalities!
- Strategy for optimization of Cu-containing contacts:
  - Understand effect of temperature on lifetime
  - Adjust Cu to optimize depletion width and  $V_{\text{oc}}$  (and limit Cu diffusion into CdS)
  - **Future work – maintain lifetime in quazi-neutral region during contacting!**

# Thank You!

