Aqueous Synthesis of ZnO for Applications in Optoelectronics

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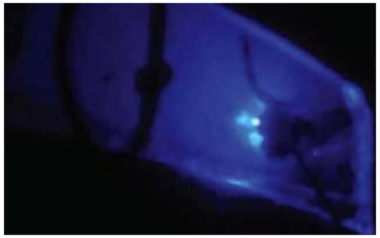
Thesis Defense

School of Engineering and Applied Sciences, Harvard University

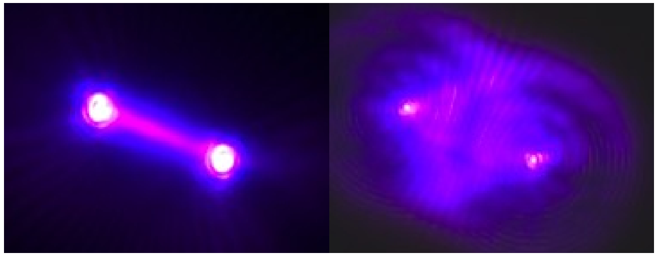
ZnO for optoelectronics

Source

ZnO LED

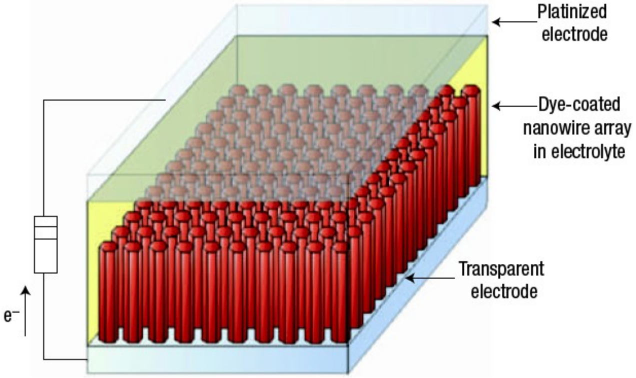


ZnO nanowire laser

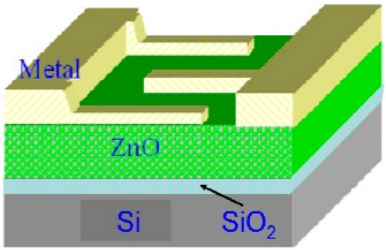


Detect

ZnO nanowire DSSC



ZnO photodetector



Manipulate

ZnO electro-optic modulator

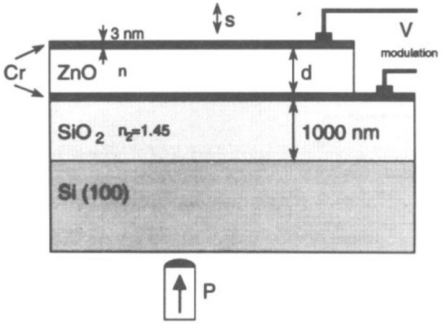
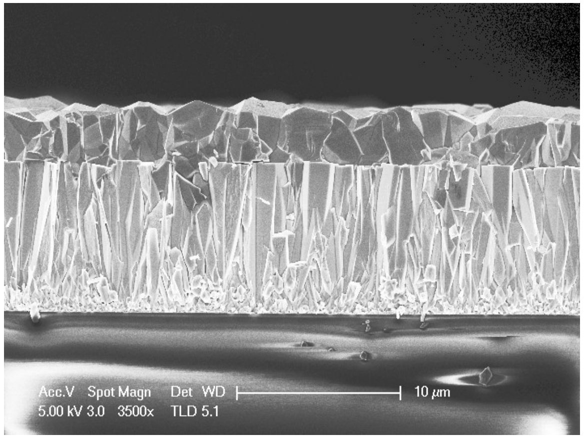


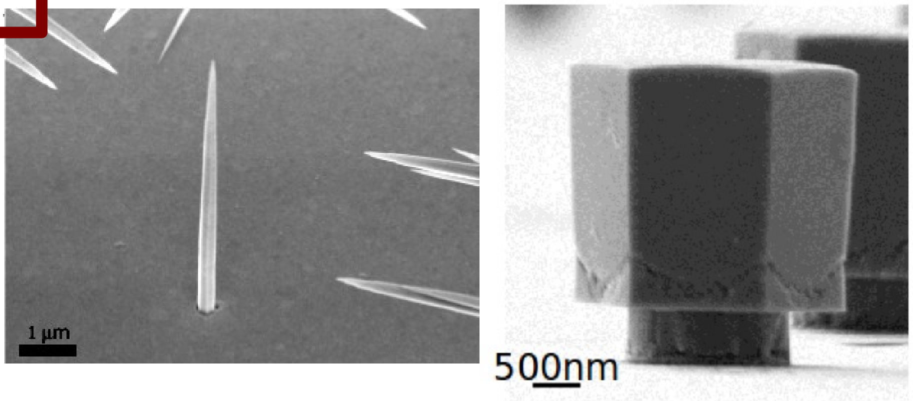
Image sources:
LED: http://www.photonics.com/Article.aspx?AID=25012
Laser: http://versteegh.webnode.nl/research/
DSSC: Law, M.; Greene, L. E.; Johnson, J. C.; Saykally, R.; Yang, P. Nat Mater 2005, 4, 455–459.

Modulator: Koch, M. H.; Timbrell, P. Y.; Lamb, R. N. Semicond. Sci. Technol. 1995, 10, 1523.
Photodetector: Liu, K.; Sakurai, M.; Aono, M. Sensors 2010, 10, 8604–8634.

Expanding the use of ZnO in optoelectronics

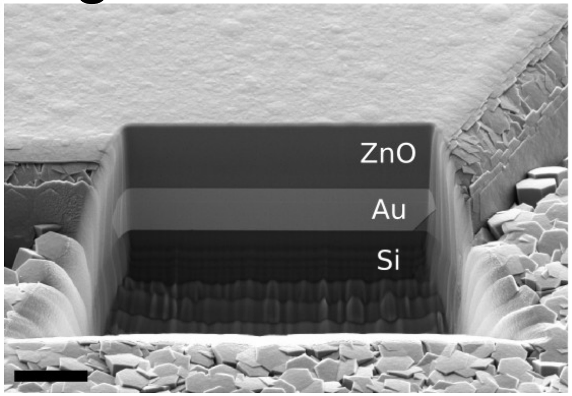


ZnO/Cu_2O
solar cells



Templated growth

Epitaxial
growth on Au



Outline

- Motivation
- Device fabrication
- Measurement techniques
- Results
  - Increased carrier collection
  - Changing behavior over time
- Discussion of mobile dopants
- Summary and Implications

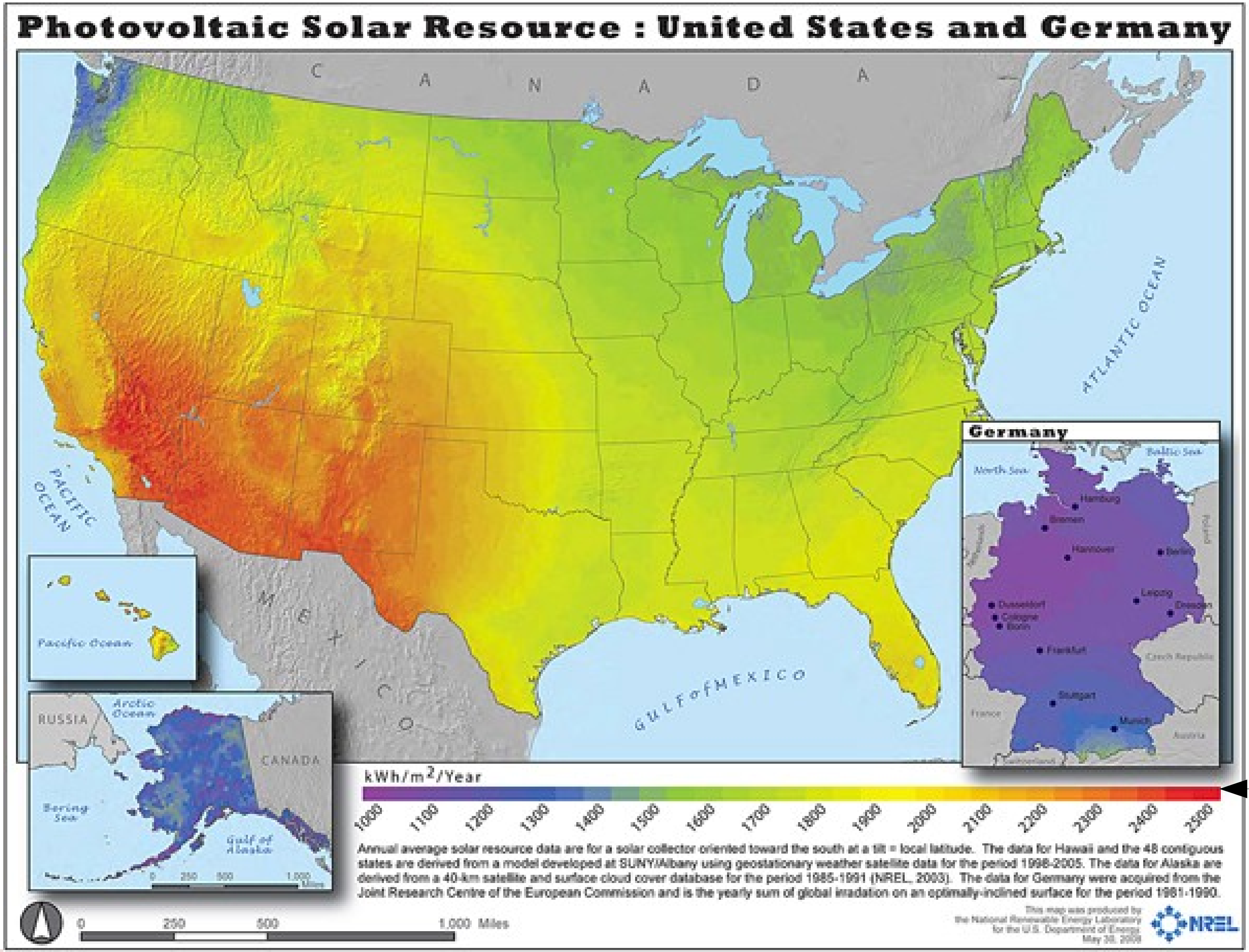
Benefits of using solar cells

Renewable energy sources

Non-renewable energy sources

In IPCC, 2011: IPCC Special Report on Renewable Energy Sources and Climate Change Mitigation. Cambridge University Press: United Kingdom and New York, NY, USA.

Benefits of using solar cells



Photovoltaic Solar Resource : United States and Germany

Annual average solar resource data are for a solar collector oriented toward the south at a tilt = local latitude. The data for Hawaii and the 48 contiguous states are derived from a model developed at SUNY/Albany using geostationary weather satellite data for the period 1998-2005. The data for Alaska are derived from a 40-km satellite and surface cloud cover database for the period 1985-1991 (NREL, 2003). The data for Germany were acquired from the Joint Research Centre of the European Commission and is the yearly sum of global irradiation on an optimally-inclined surface for the period 1981-1990.

This map was produced by the National Renewable Energy Laboratory for the U.S. Department of Energy May 30, 2008

kWh/m^2/Year

National Renewable Energy Laboratory, 5/30/2008, via Thurston Energy.

Benefits of using solar cells

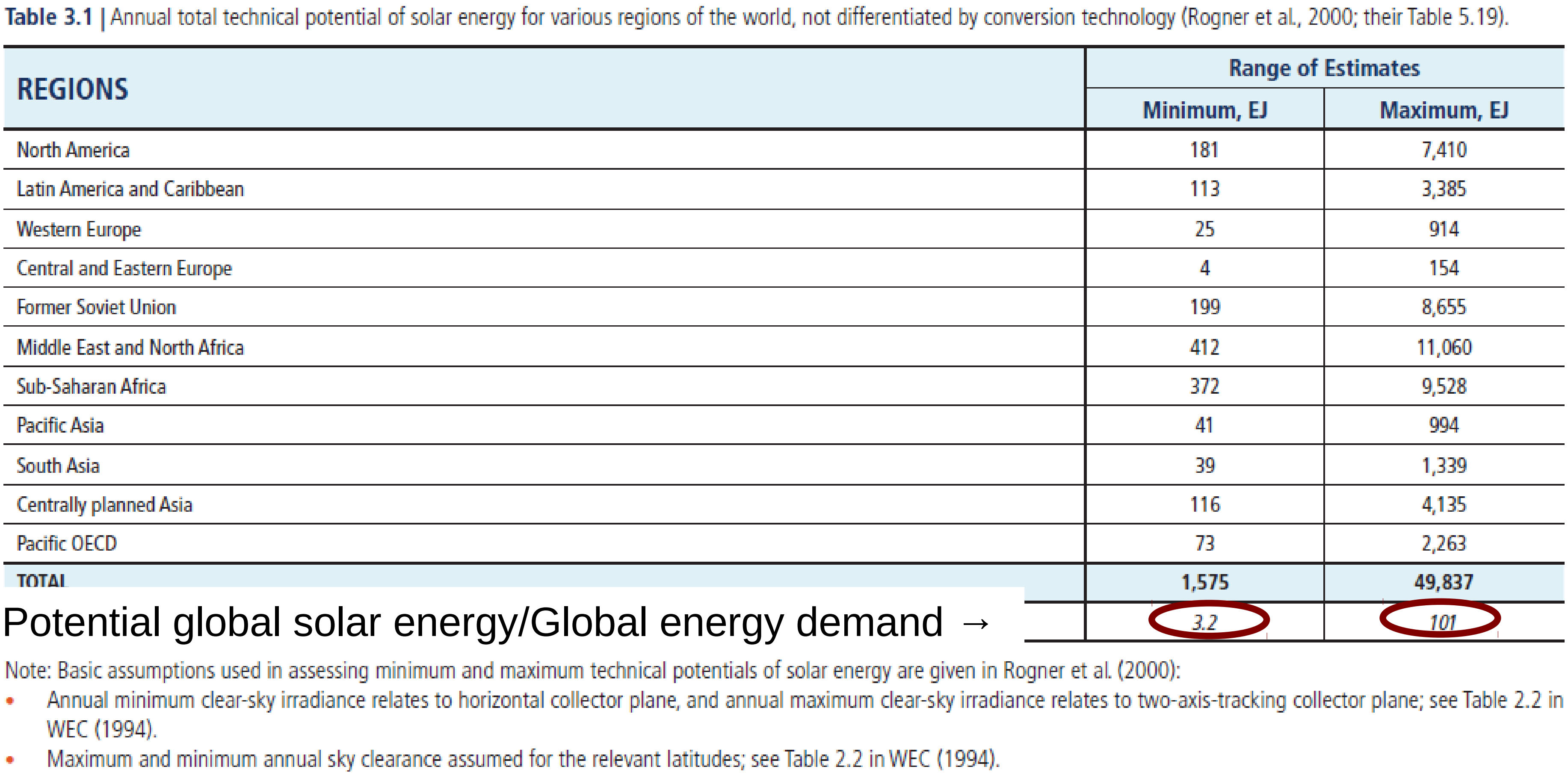


Table 3.1 | Annual total technical potential of solar energy for various regions of the world, not differentiated by conversion technology (Rogner et al., 2000; their Table 5.19).

REGIONS	**Range of Estimates**	
	Minimum, EJ	**Maximum, EJ**
North America	181	7,410
Latin America and Caribbean	113	3,385
Western Europe	25	914
Central and Eastern Europe	4	154
Former Soviet Union	199	8,655
Middle East and North Africa	412	11,060
Sub-Saharan Africa	372	9,528
Pacific Asia	41	994
South Asia	39	1,339
Centrally planned Asia	116	4,135
Pacific OECD	73	2,263
TOTAL	**1,575**	**49,837**
Potential global solar energy/Global energy demand →	*3.2*	*101*

Note: Basic assumptions used in assessing minimum and maximum technical potentials of solar energy are given in Rogner et al. (2000):

- Annual minimum clear-sky irradiance relates to horizontal collector plane, and annual maximum clear-sky irradiance relates to two-axis-tracking collector plane; see Table 2.2 in WEC (1994).
- Maximum and minimum annual sky clearance assumed for the relevant latitudes; see Table 2.2 in WEC (1994).

In IPCC, 2011: IPCC Special Report on Renewable Energy Sources and Climate Change Mitigation. Cambridge University Press: United Kingdom and New York, NY, USA.

Benefits of using solar cells

- Clean energy source
- Domestic energy source
- Abundant energy source
- Save petroleum for other of humanity's needs

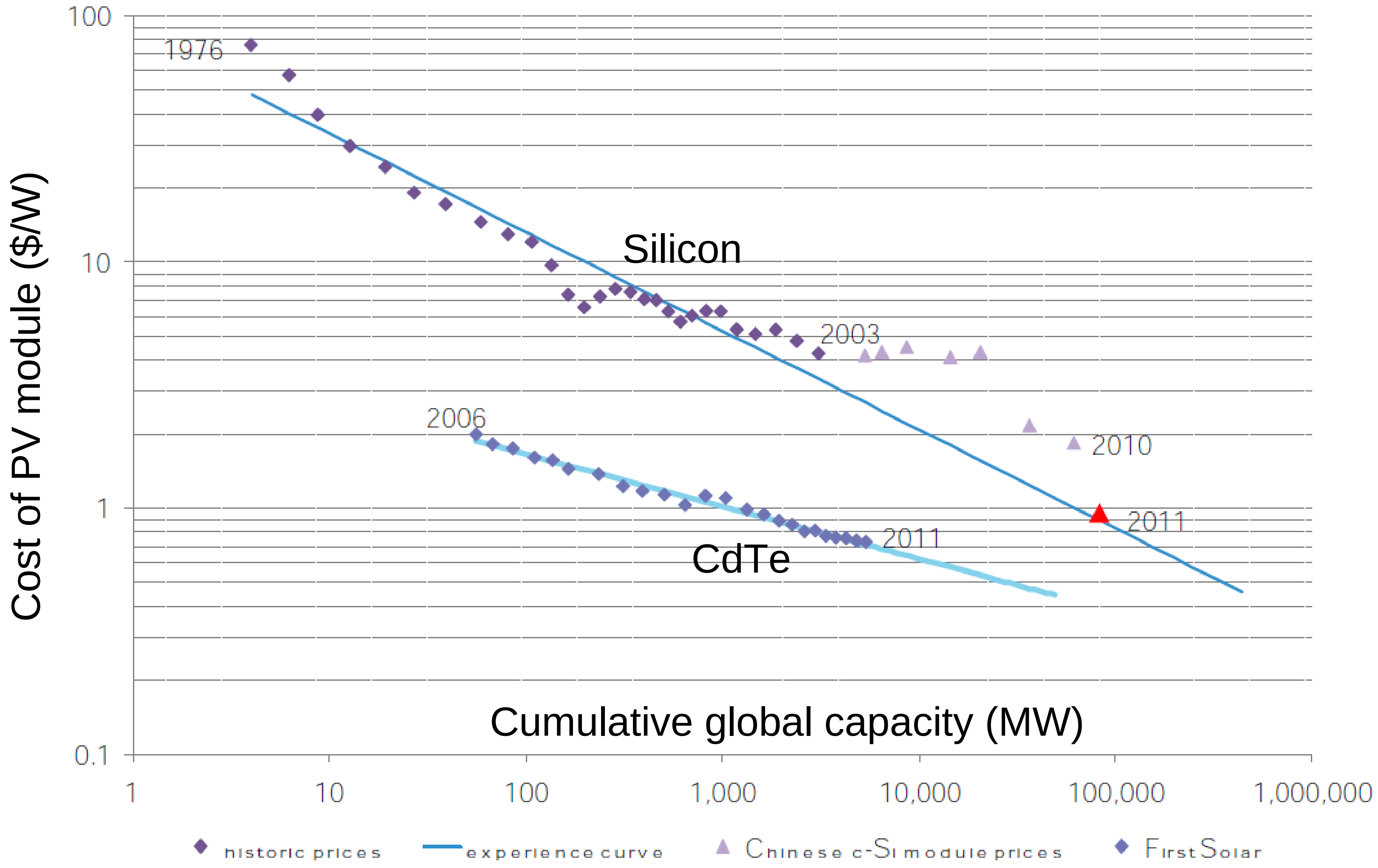
Solvents
Bearing Grease
Ink
Floor Wax
Ballpoint Pens
Football Cleats
Upholstery
Sweaters
Boats
Insecticides

Bicycle Tires
Sports Car Bodies
Nail Polish
Fishing lures
Dresses
Tires
Golf Bags
Perfumes
Cassettes
Purses

Dishwasher parts
Tool Boxes
Shoe Polish
Motorcycle Helmet
Caulking
Petroleum Jelly
Transparent Tape
CD Player
Faucet Washers

Antiseptics
Clothesline
Curtains
Food Preservatives
Basketballs
Soap
Vitamin Capsules
Antihistamines
Aspirin

Current economic state of solar cells



"Reconsidering the Economics of Photovoltaic Power", Bloomberg New Finance, March 16, 2012.

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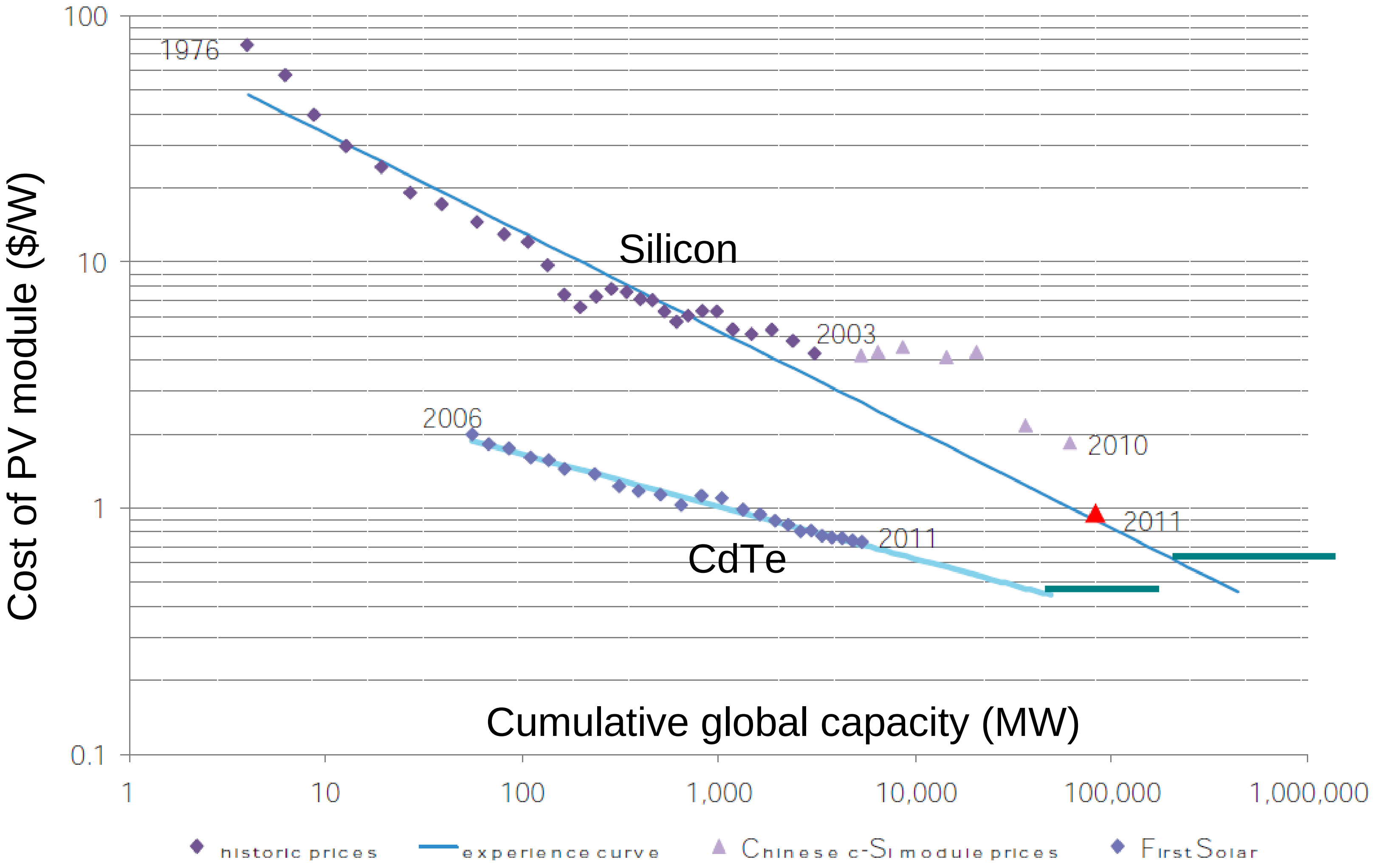
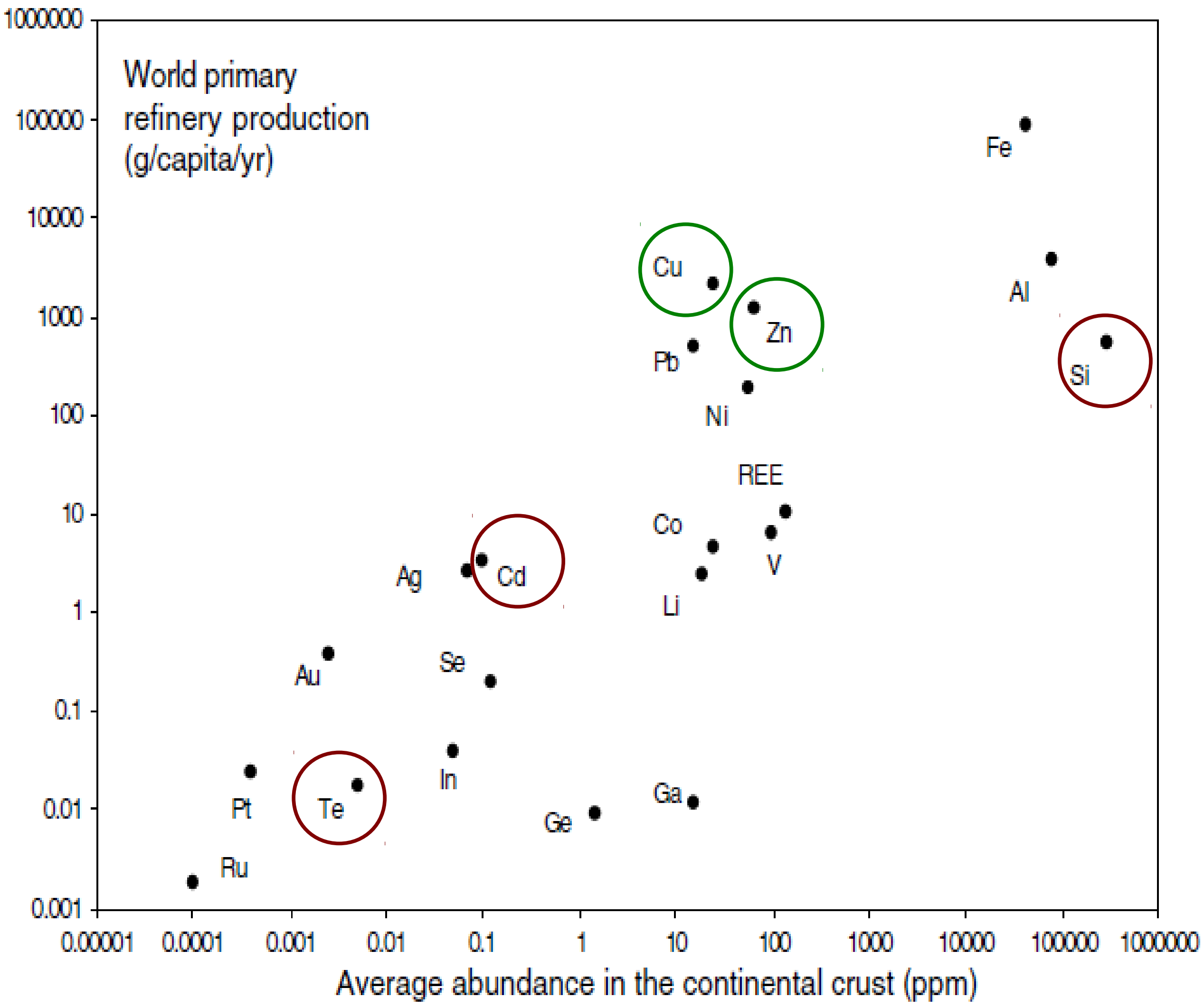


"Reconsidering the Economics of Photovoltaic Power", Bloomberg New Finance, March 16, 2012.

Limitations in materials

Predominant ore	ΔG_f (kJ/mol)
SiO_2	-856.4
$CuFeS_2$	-224.5



USGS (2000). *Mineral Commodity Summaries 2000*. U.S. Dept. of the Interior, Geological Survey, Reston.
Wedepohl, K. H. (1995). The Composition of the continental crust. *Geochimica et Cosmochimica Acta* 59(7): 1217-1232.
Andersson, B. A. (2000) Materials availability for large-scale thin-film photovoltaics. *Progress in Photovoltaics,* 8**,** 61-76.

Cu_2O/ZnO

Cu_2O

- E_g=2.0 eV
- Self-doped p-type material by V_{cu}
- Inexpensive, abundant
- Easy to deposit polycrystalline through electrodeposition

(1) Nishi, Y.; Miyata, T.; Minami, T. Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films 2012, 30, 04D103.

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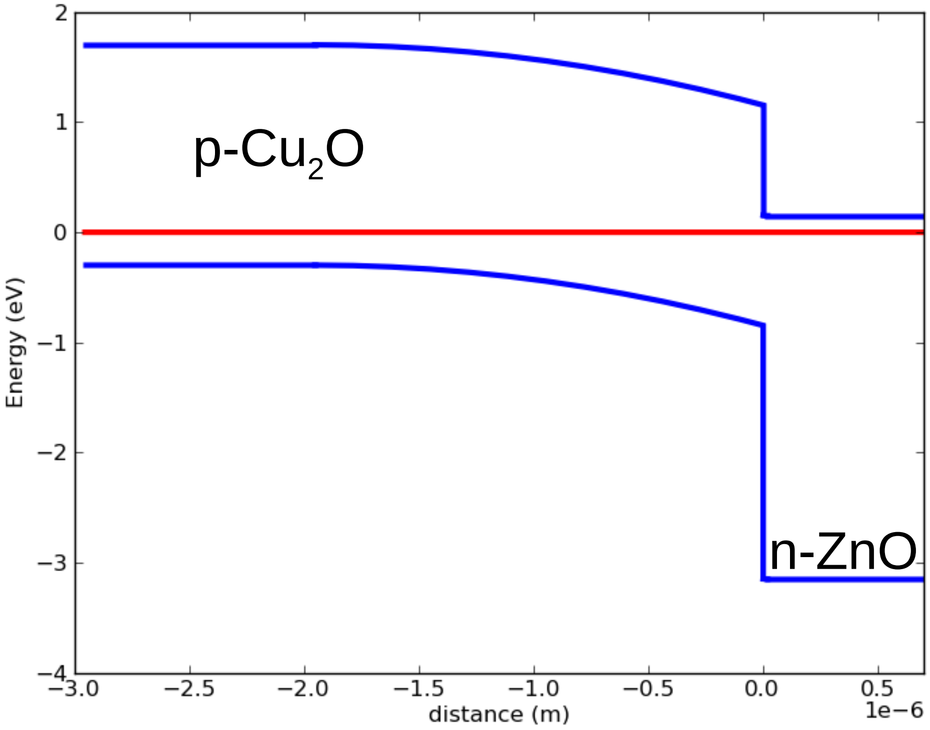
- Wide bandgap E_g = 3.4 eV
- Type II heterojunction



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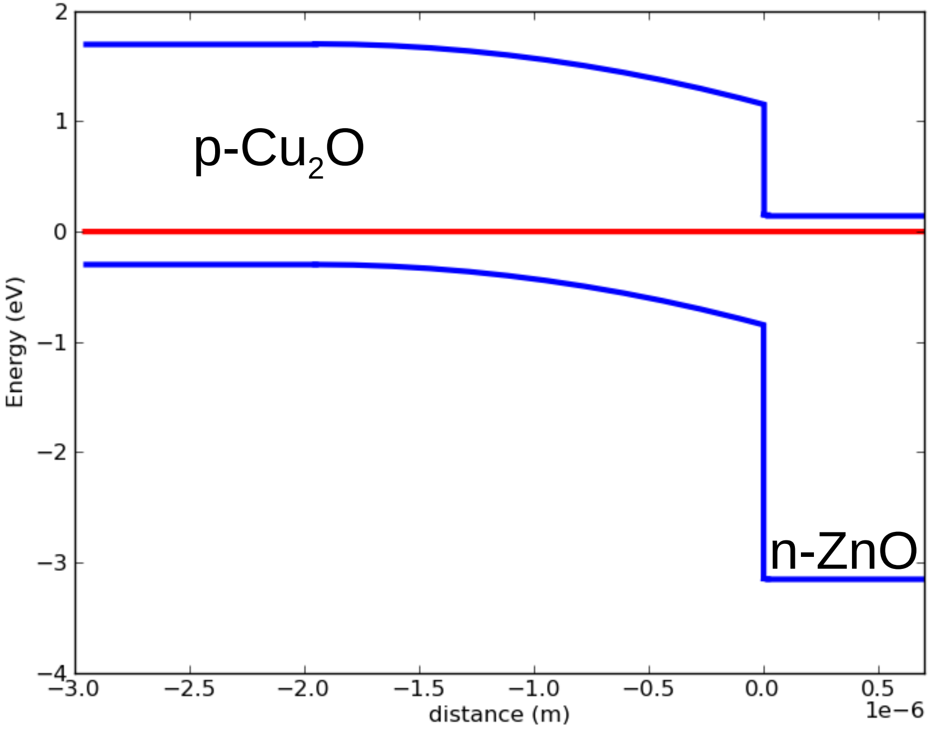


Theoretical efficiency ~13%. Current record ~4%.[1]

(1) Nishi, Y.; Miyata, T.; Minami, T. Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films 2012, 30, 04D103.

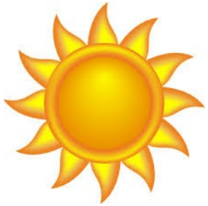
Radial junction/3D solar cells

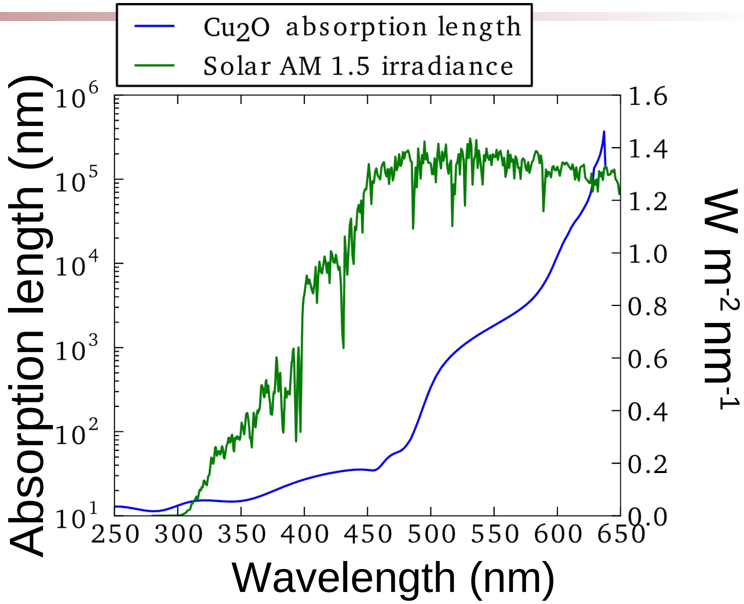
Absorption length = α_L

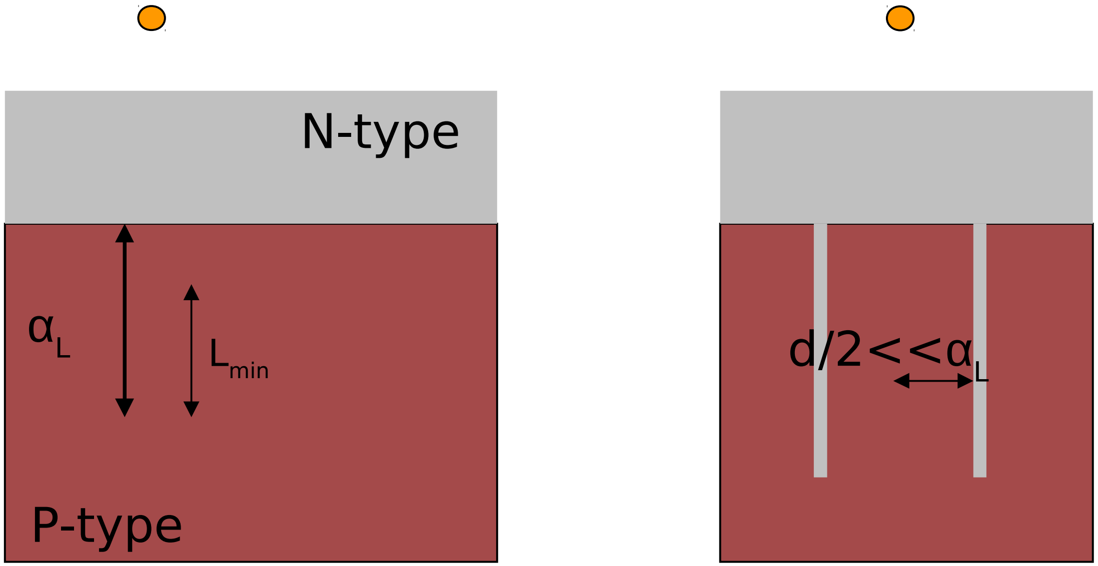
Minority carrier diffusion length = L_{min}

Recombination → Lost photocurrent

A common design constraint: Total thickness< L_{min}







For electrodeposited Cu_2O:

L_{min} ~ 100nm [1]

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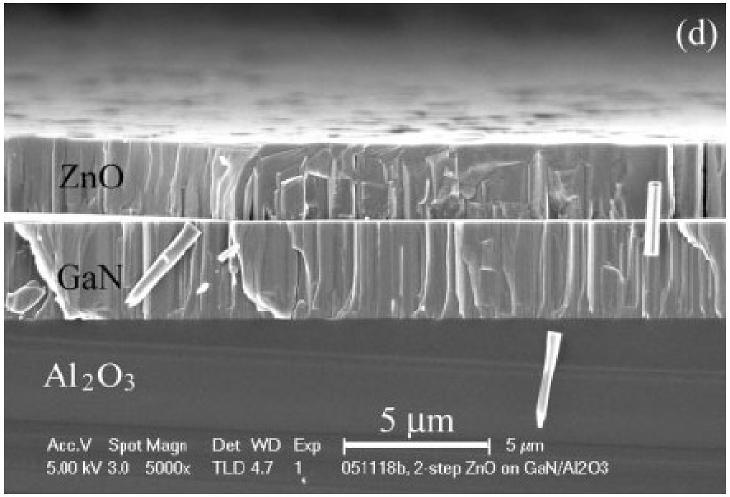
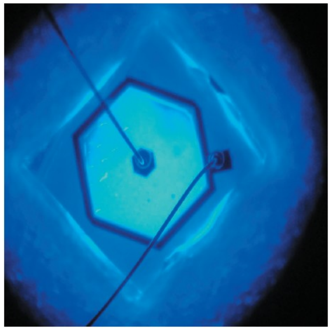
(1) Musselman, K. P.; Ievskaya, Y.; MacManus-Driscoll, J. L. Applied Physics Letters 2012, 101, 253503–253503–5.

(2) Absorption length derived from data in Malerba, C.; Biccari, F.; Leonor Azanza Ricardo, C.; D'Incau, M.; Scardi, P.; Mittiga, A. Solar Energy Materials and Solar Cells 2011, 95, 2848–2854.

ZnO aqueous solution growth





Thompson, D. B.; Richardson, J. J.; DenBaars, S. P.; Lange, F. F. Applied Physics Express 2009, 2, 042101.
Kim, J. H.; Kim, E.-M.; Andeen, D.; Thomson, D.; DenBaars, S. P.; Lange, F. F. Advanced Functional Materials 2007, 17, 463–471.

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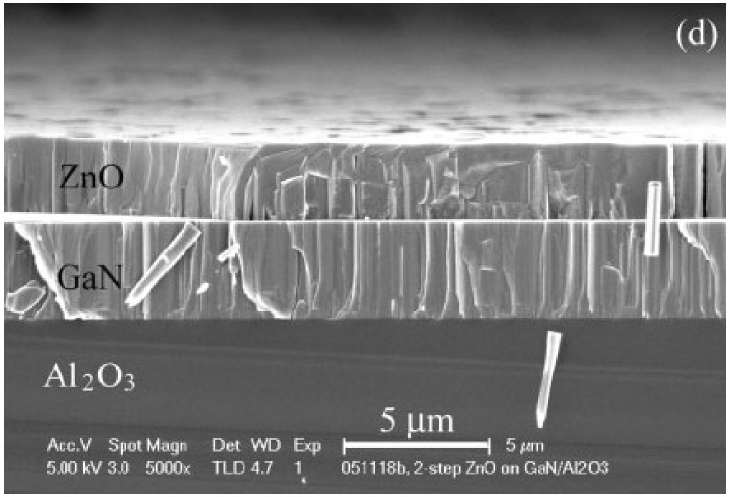
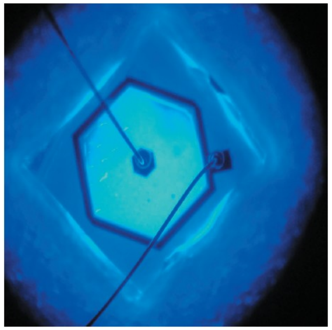
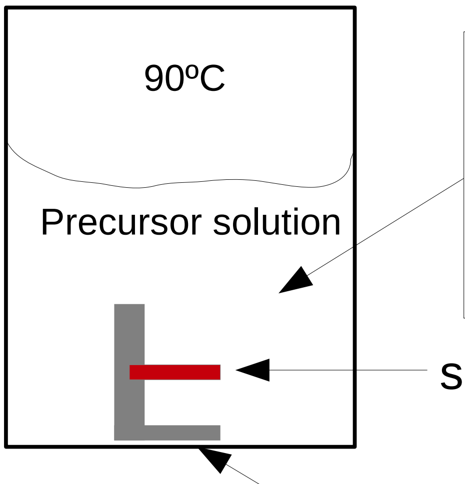






Teflon container

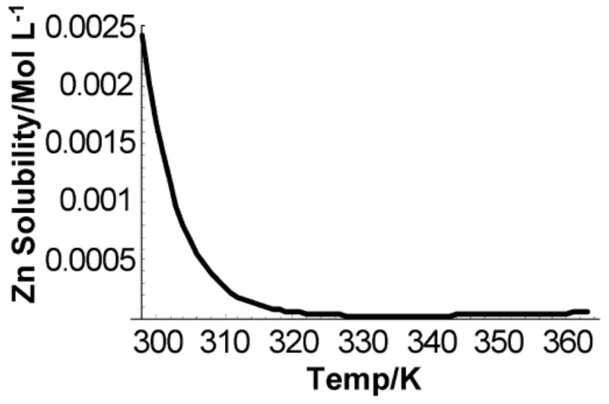
90ºC

Precursor solution

Zn salt source,
water,
acid/base to adjust pH,
complexing agent,
surface active agent

sample

Sample holder



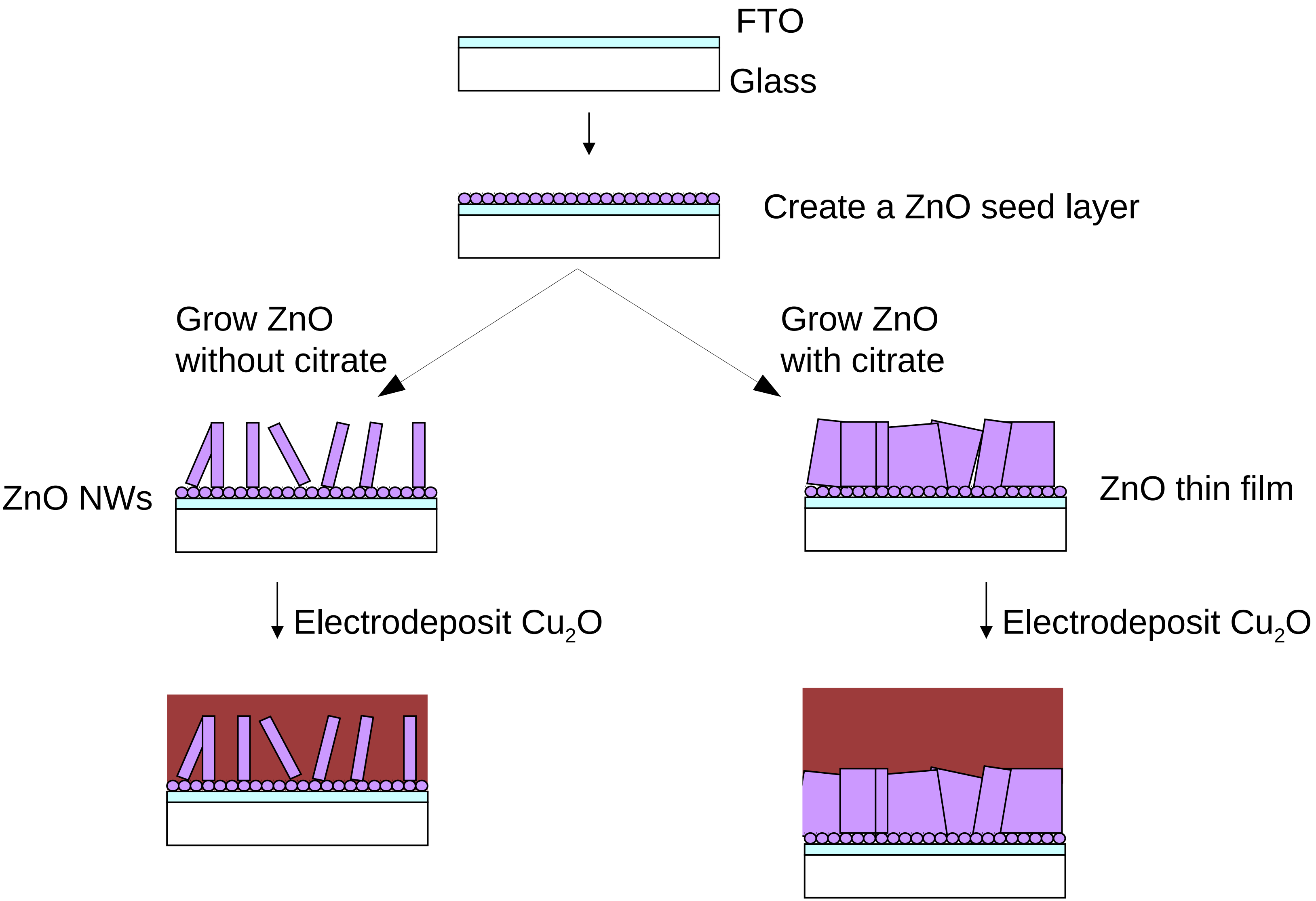
Richardson, J. J.; Lange, F. F. Journal of Materials Chemistry 2011, 21, 1859–1865.

With addition of ***ammonia***, zinc solubility decreases with increasing temperature!

Richardson, J. J.; Lange, F. F. Crystal Growth & Design 2009, 9, 2570–2575.

Thompson, D. B.; Richardson, J. J.; DenBaars, S. P.; Lange, F. F. Applied Physics Express 2009, 2, 042101.
Kim, J. H.; Kim, E.-M.; Andeen, D.; Thomson, D.; DenBaars, S. P.; Lange, F. F. Advanced Functional Materials 2007, 17, 463–471.

Plan of making ZnO/Cu_2O solar cells



FTO

Glass

Create a ZnO seed layer

Grow ZnO
without citrate

Grow ZnO
with citrate

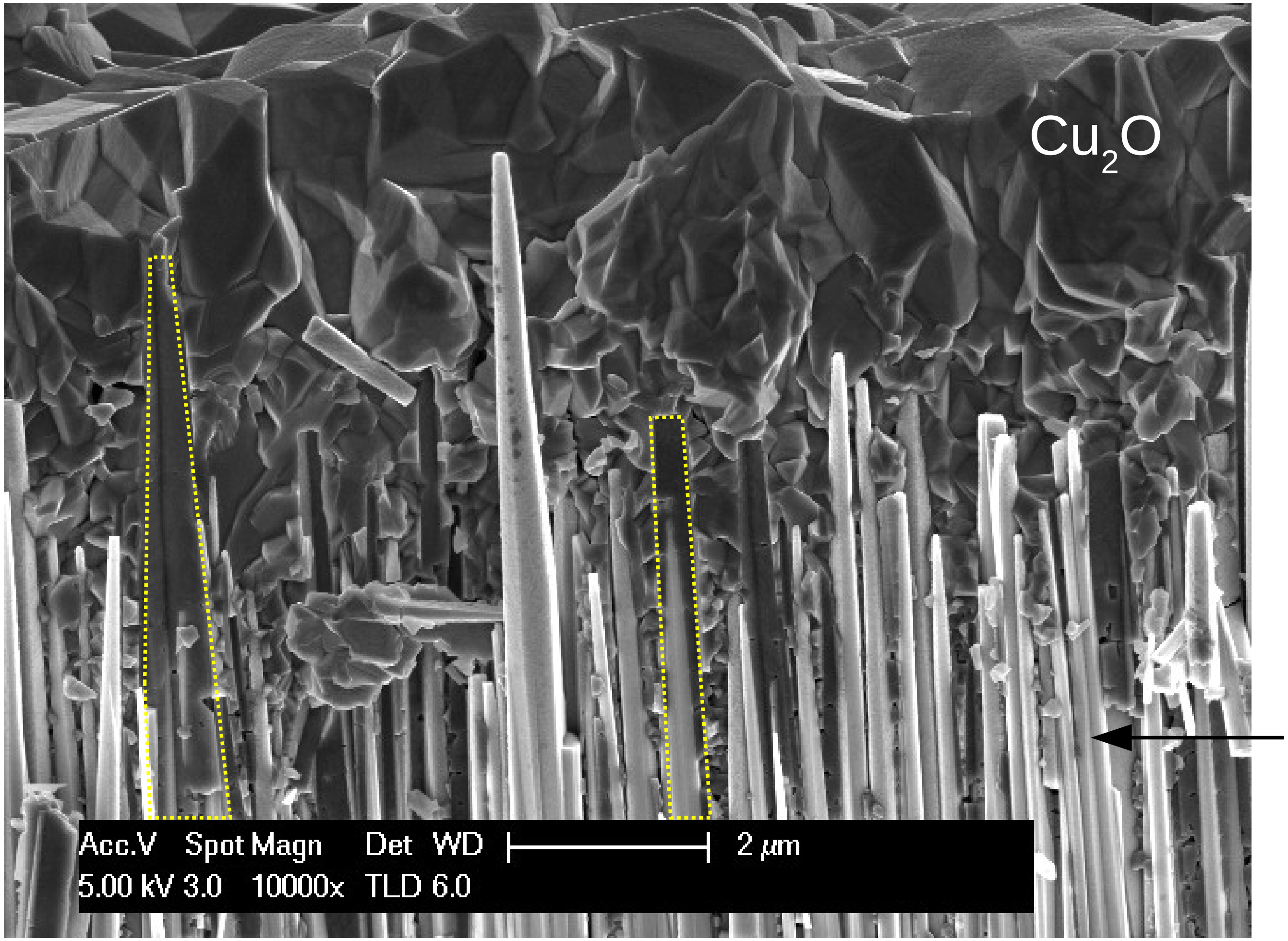
ZnO NWs

ZnO thin film

Electrodeposit Cu_2O

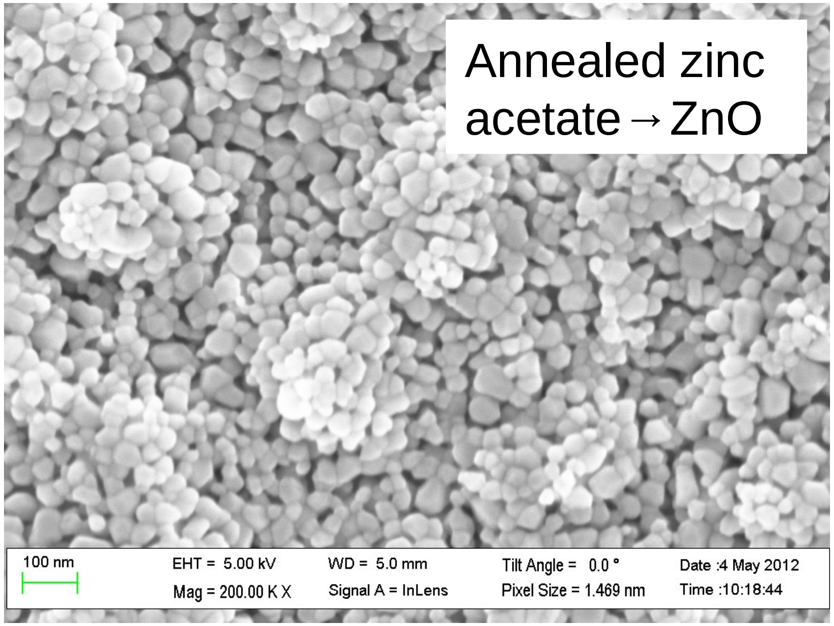
Electrodeposit Cu_2O

First attempts at ZnO/Cu_2O solar cells



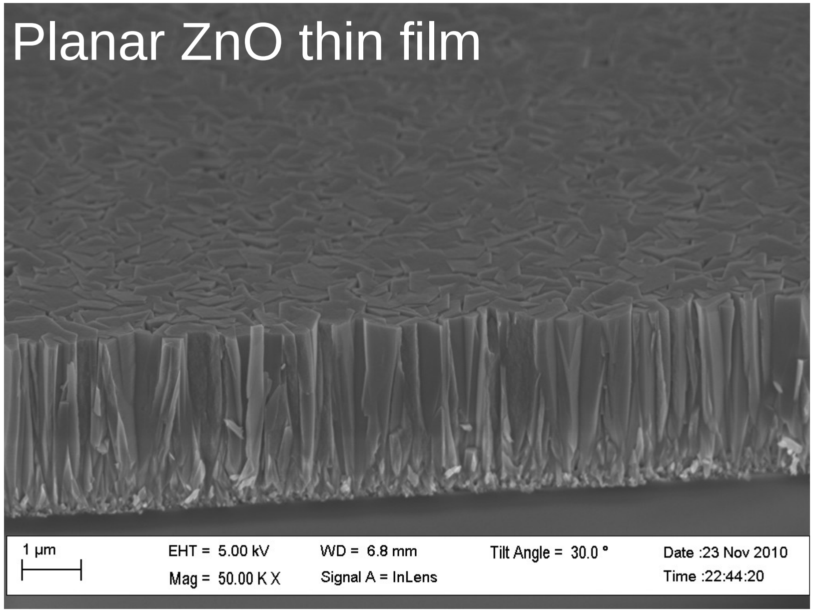
Not enough space between ZnO wires for Cu_2O.

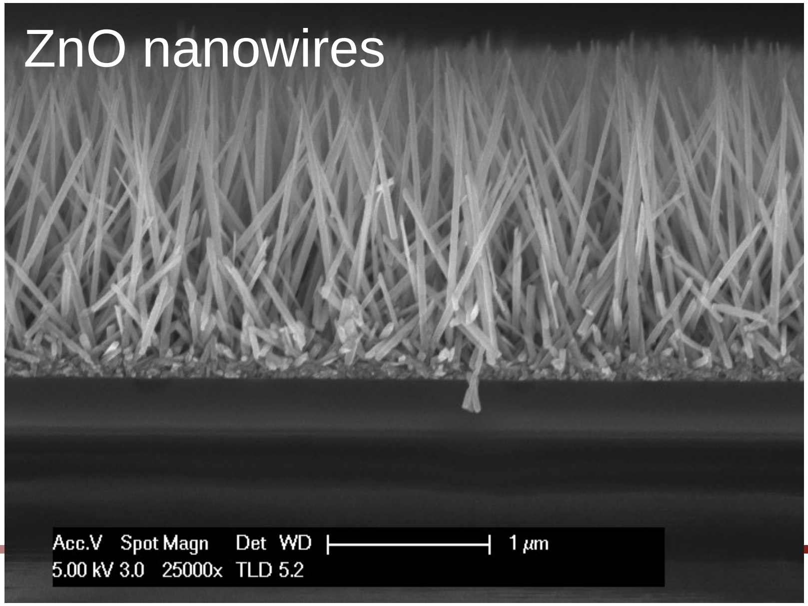
Changed seeding to make nanowires


Annealed zinc acetate → ZnO

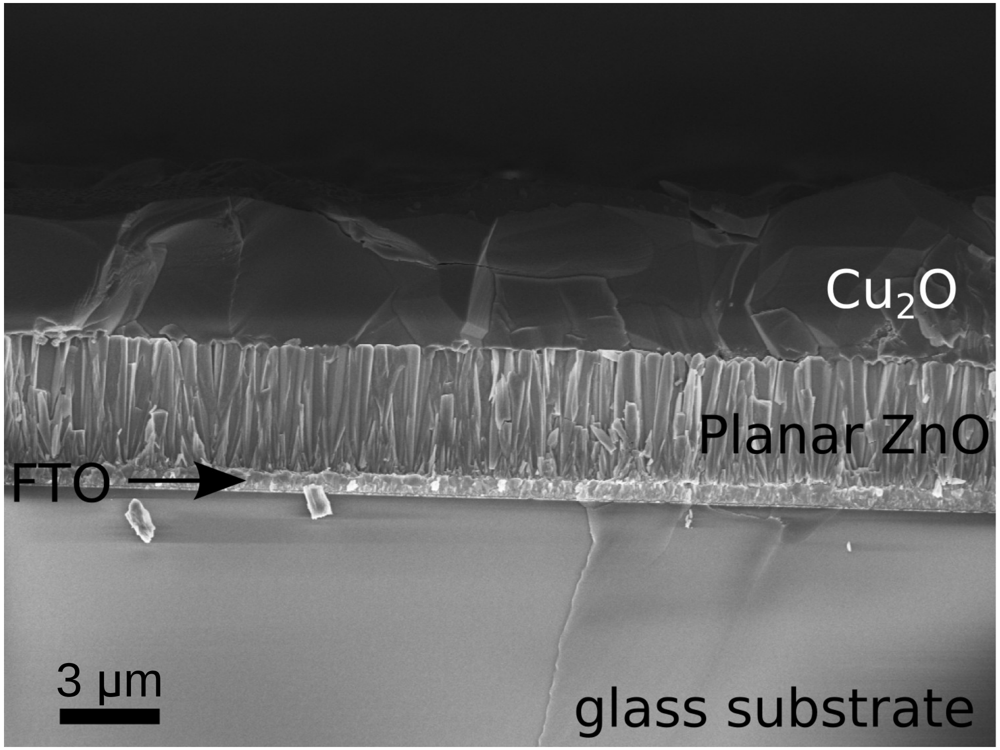
Seed size controls the diameter of the nanowire.

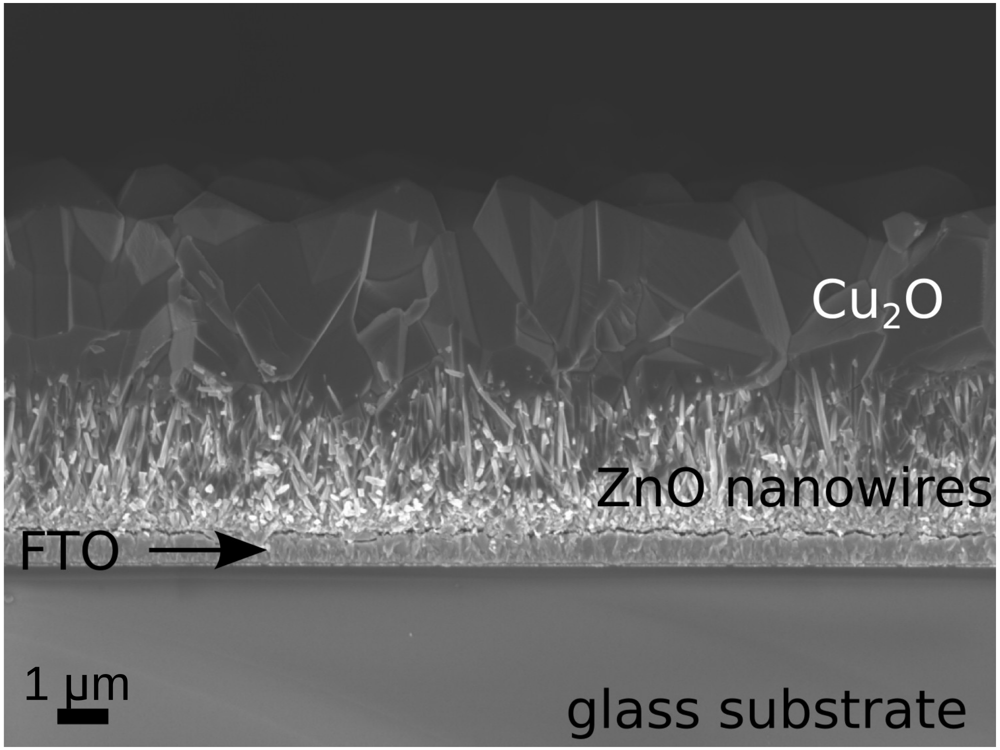
Thinner wires!


Planar ZnO thin film

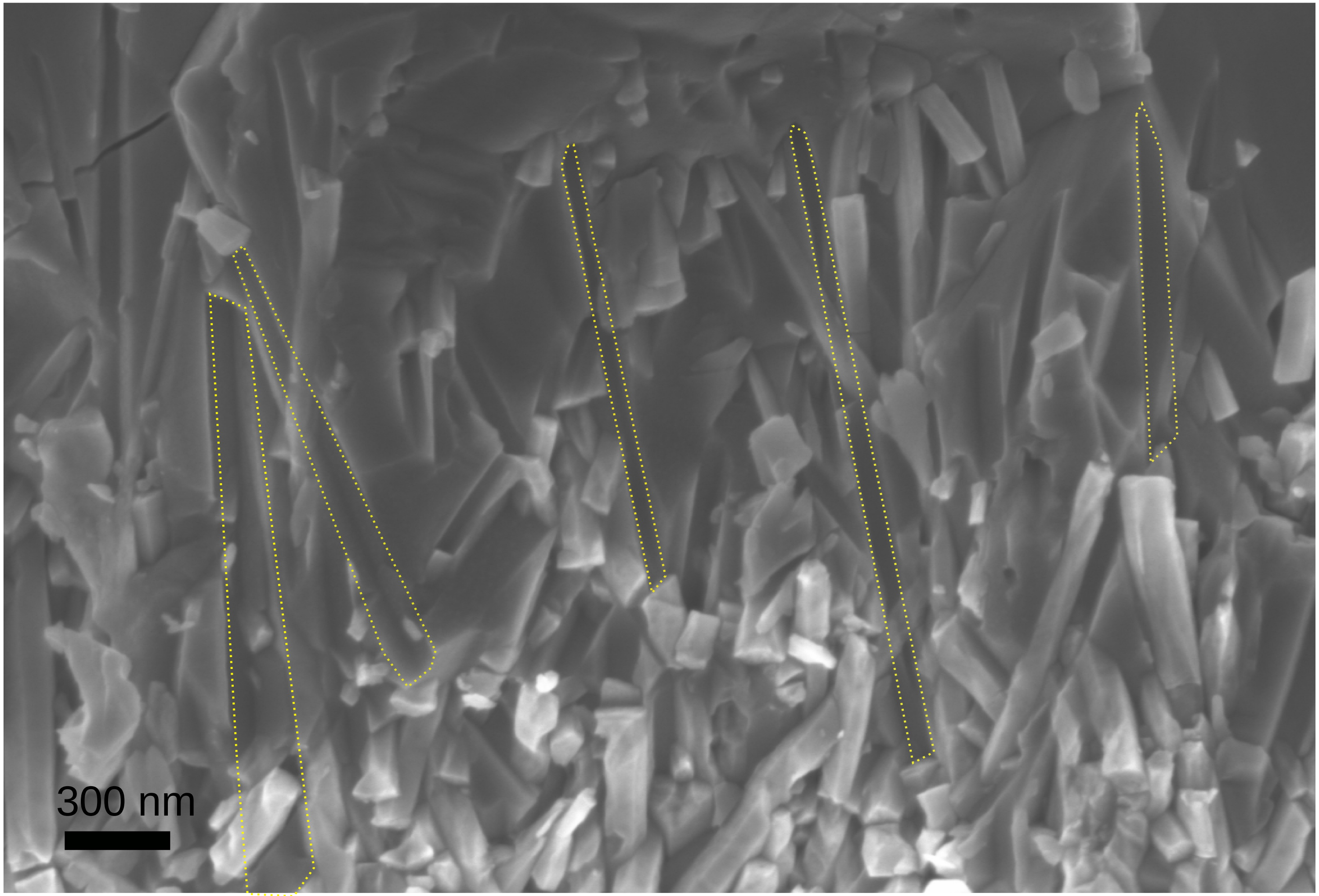

ZnO nanowires

Planar and NW solar cells





NW impressions in Cu_2O matrix



Ideal solar cell formation

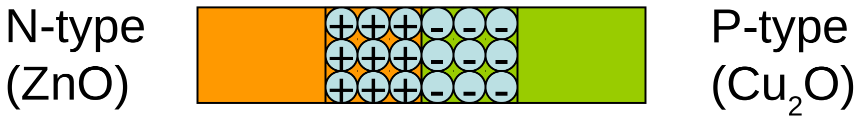
Form a p-n junction

n-type

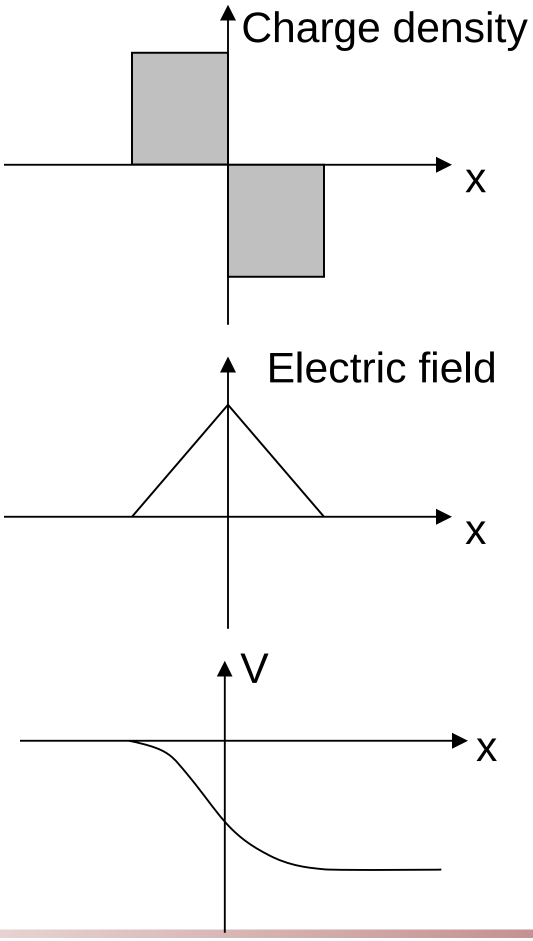
p-type

Internal electric field in a p-n junction

Form a p-n junction



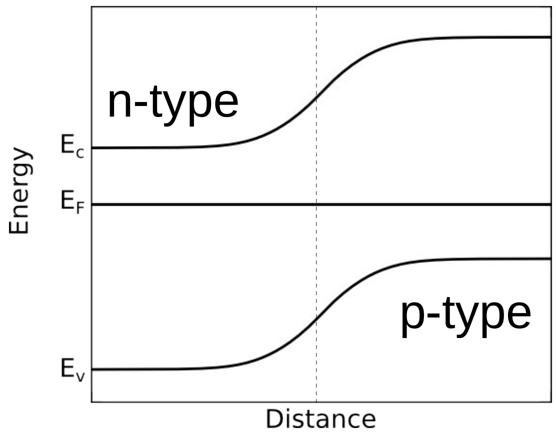
As electrons and holes move to achieve equilibrium, they leave behind charged ions.



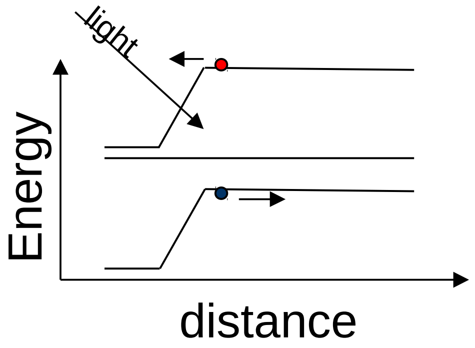
$$\frac{d\vec{E}}{dx} = \frac{\rho}{\varepsilon}$$

$$\frac{dV}{dx} = -\vec{E}$$

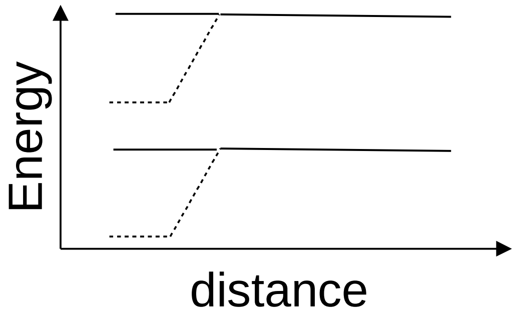
Energy = -qV



Measuring current-voltage

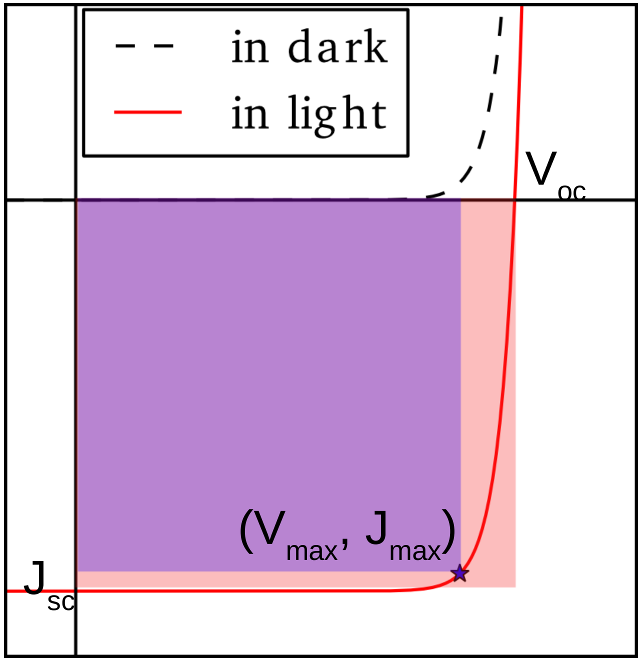


- I_{sc} : short circuit current.
- Measure of photon absorption and carrier collection.



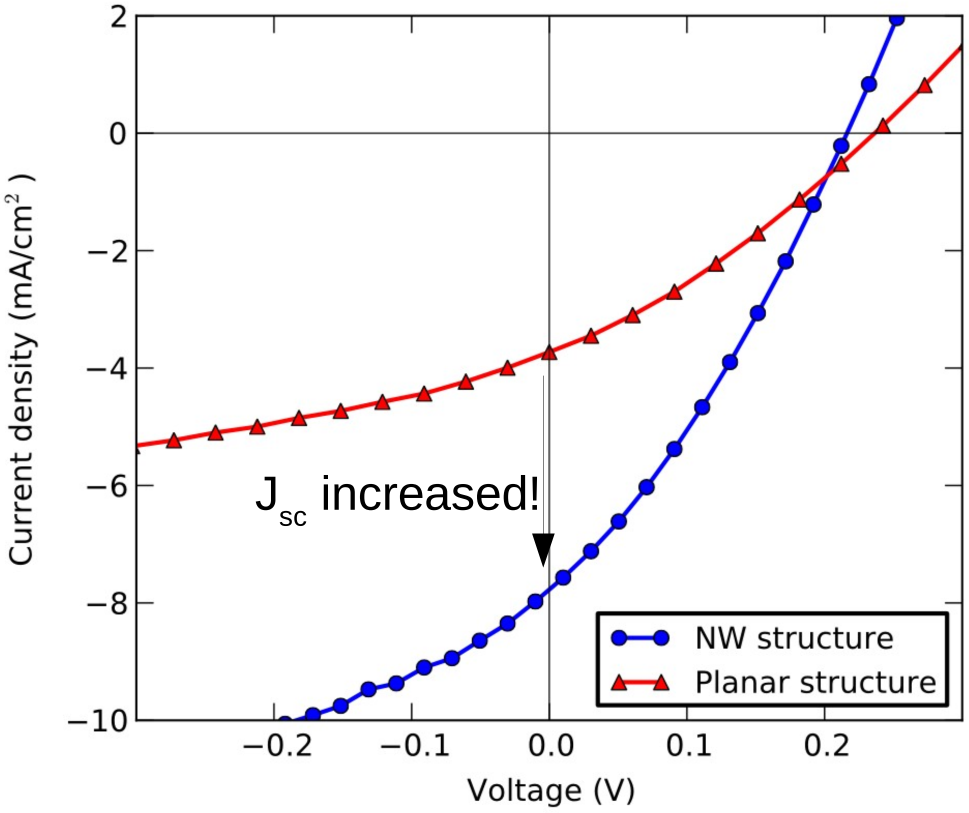
- V_{oc} : open circuit voltage.
- Measure of built-in voltage.

Fill factor, FF = $(J_{max}V_{max})/(J_{sc}V_{oc})$



$P_{max}=J_{sc}V_{oc}FF$

Enhanced carrier collection: J_{sc}



Planar ZnO on FTO

J_{sc} = 4.1 mA/cm²

V_{oc} = 0.236 V

FF = 0.305

Eff = 0.30%

NW ZnO on FTO

J_{sc} = 8.5 mA/cm²

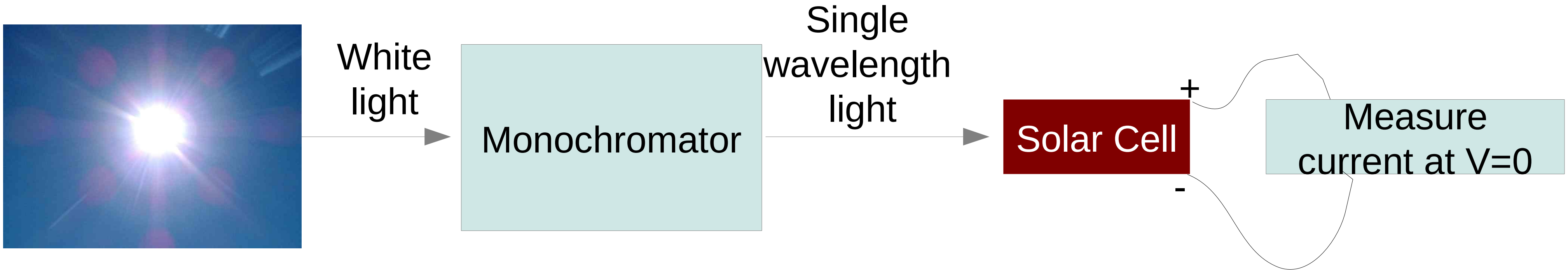
V_{oc} = 0.216 V

FF = 0.308

Eff = 0.57%

Nanowires increased carrier collection, indicated by increased J_{sc}.

External quantum efficiency



$$\mathrm{EQE} = \frac{\#\ \text{electrons collected}\ (\lambda)}{\#\ \text{photons incident}\ (\lambda)}$$

$$= (\mathit{absorption\ probability})\, x\, (\mathit{carrier\ collection\ probability})$$

External Quantum Efficiency

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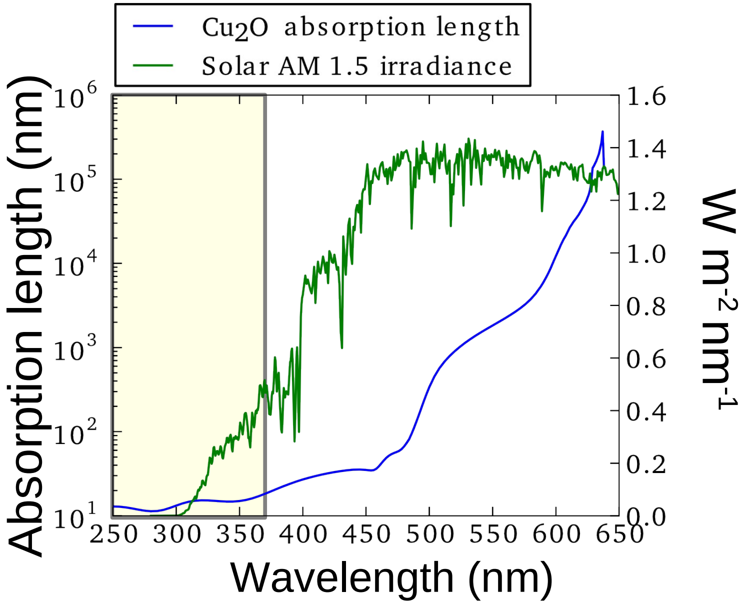

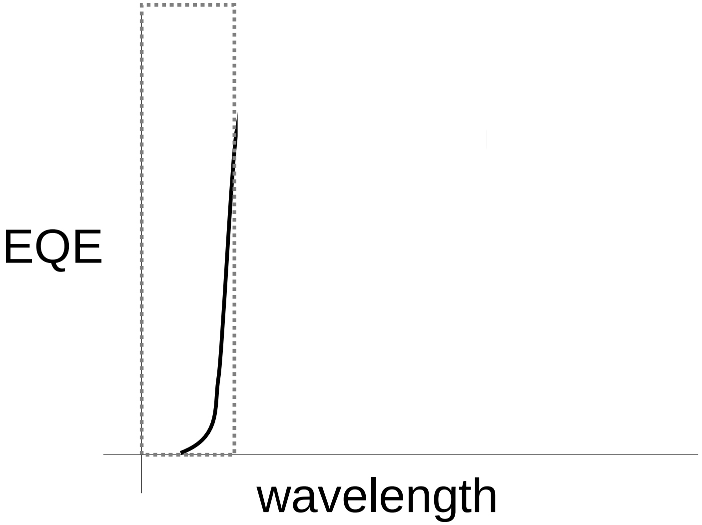

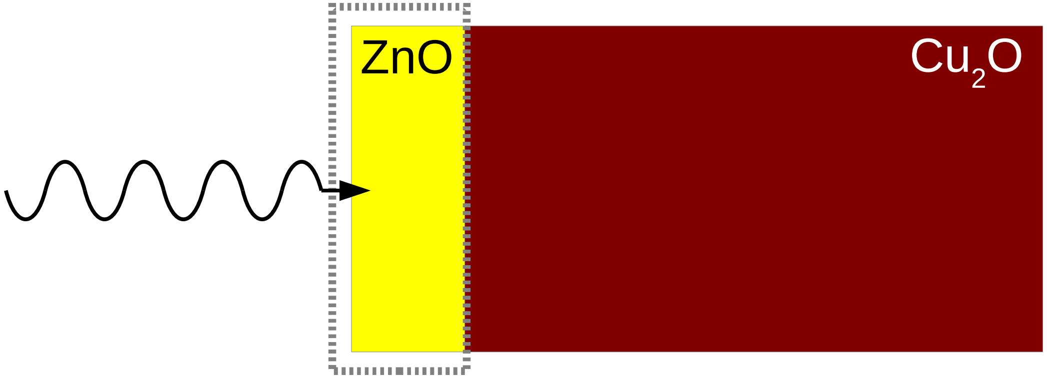

Absorption length derived from data in Malerba, C.; Biccari, F.; Leonor Azanza Ricardo, C.; D'Incau, M.; Scardi, P.; Mittiga, A. Solar Energy Materials and Solar Cells 2011, 95, 2848–2854.

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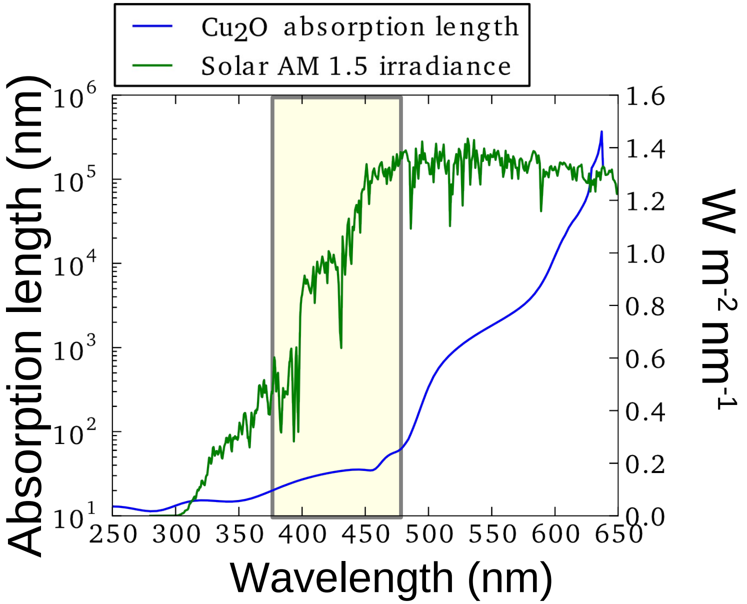

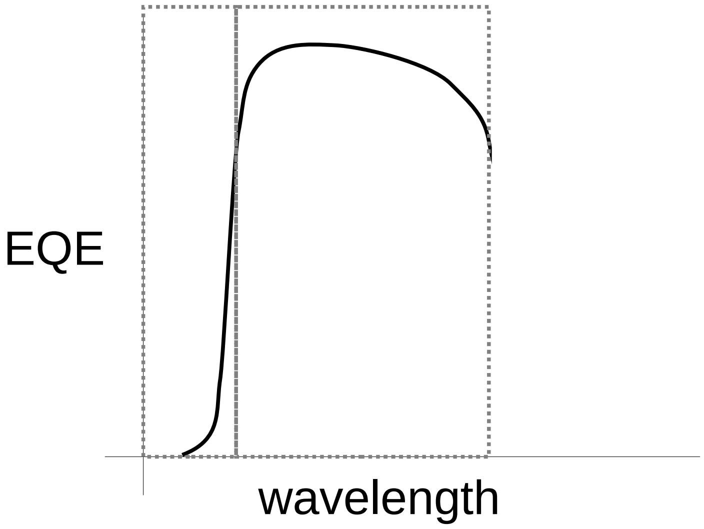

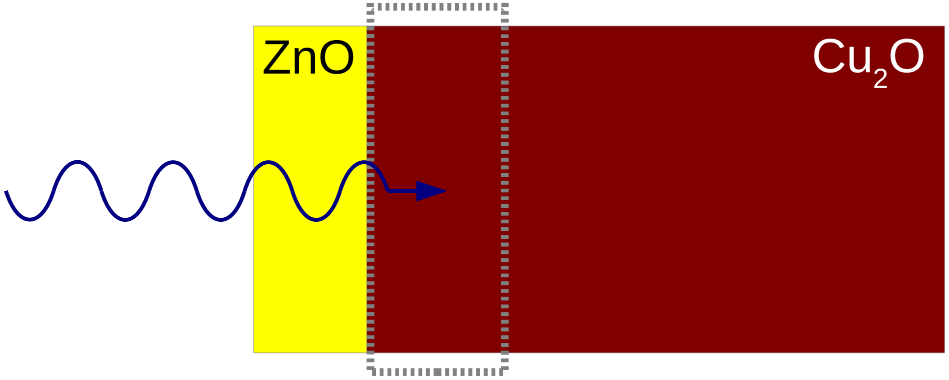

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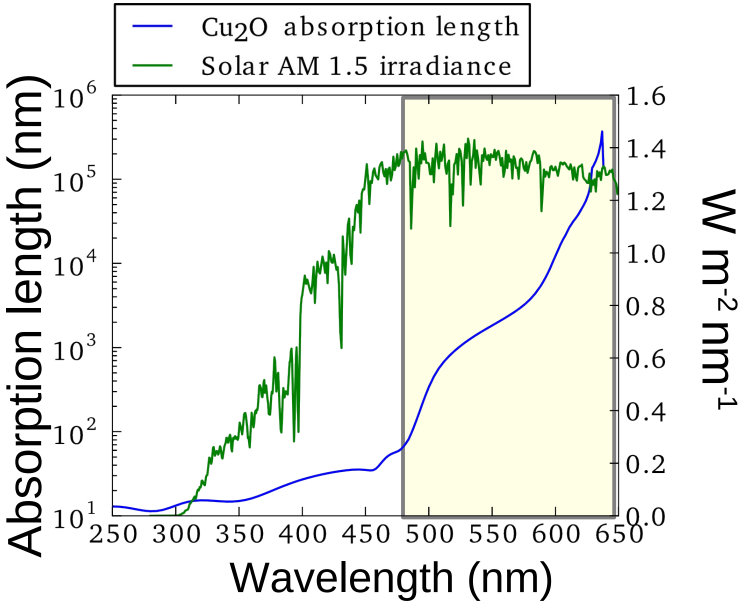
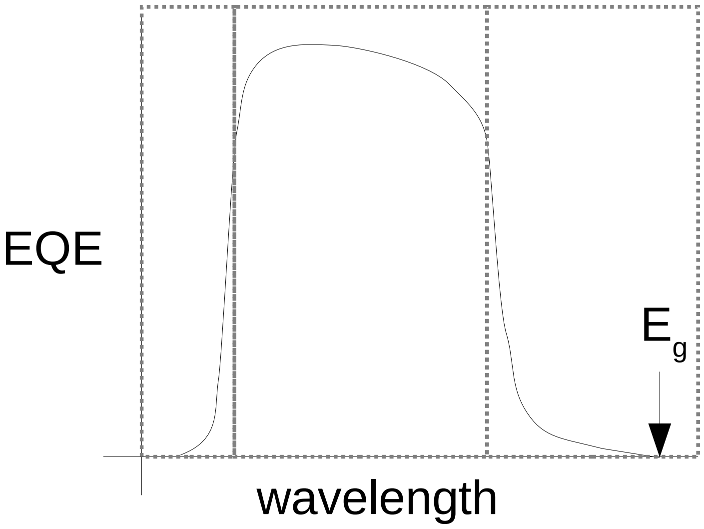
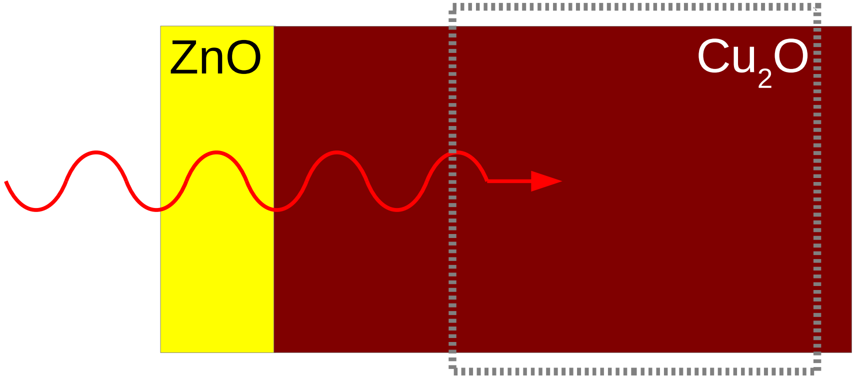
$$\mathrm{EQE} = \frac{\#\ \text{electrons collected}\ (\lambda)}{\#\ \text{photons incident}\ (\lambda)}$$

$$= (\textit{absorption probability})\, x\, (\textit{carrier collection probability})$$

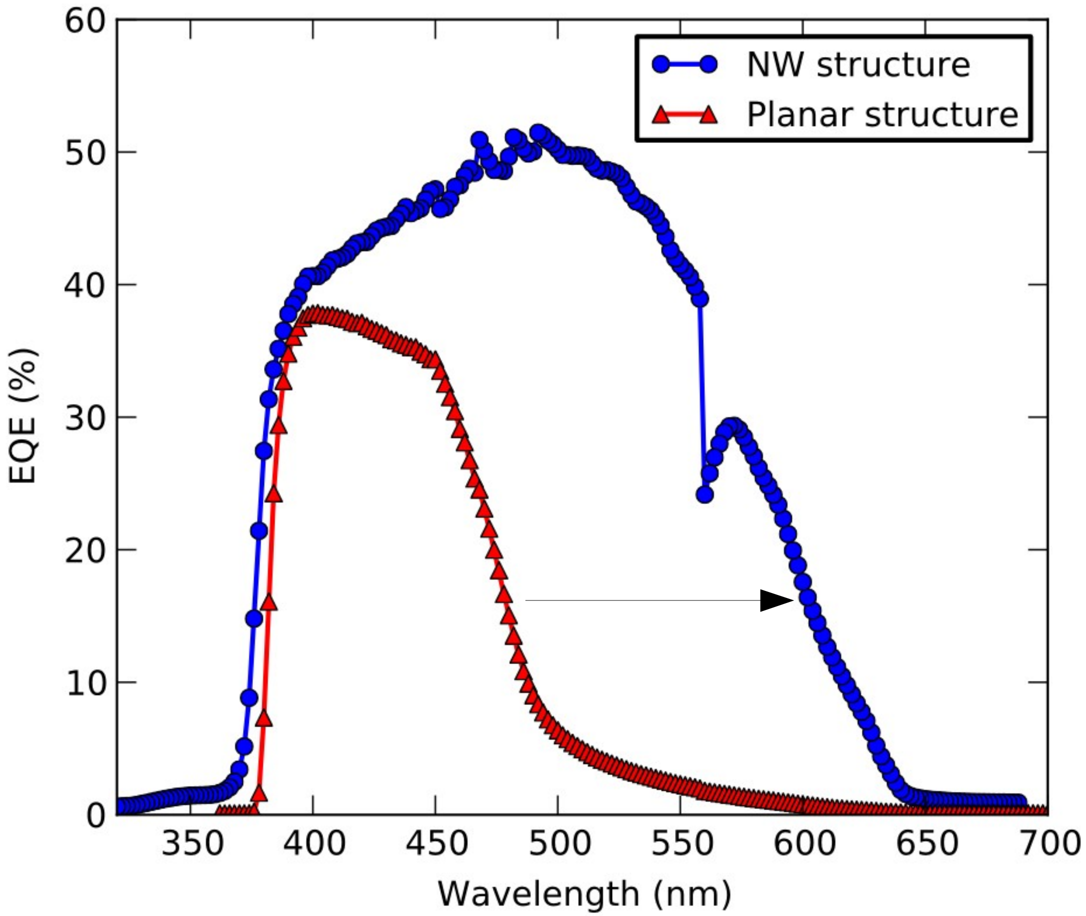


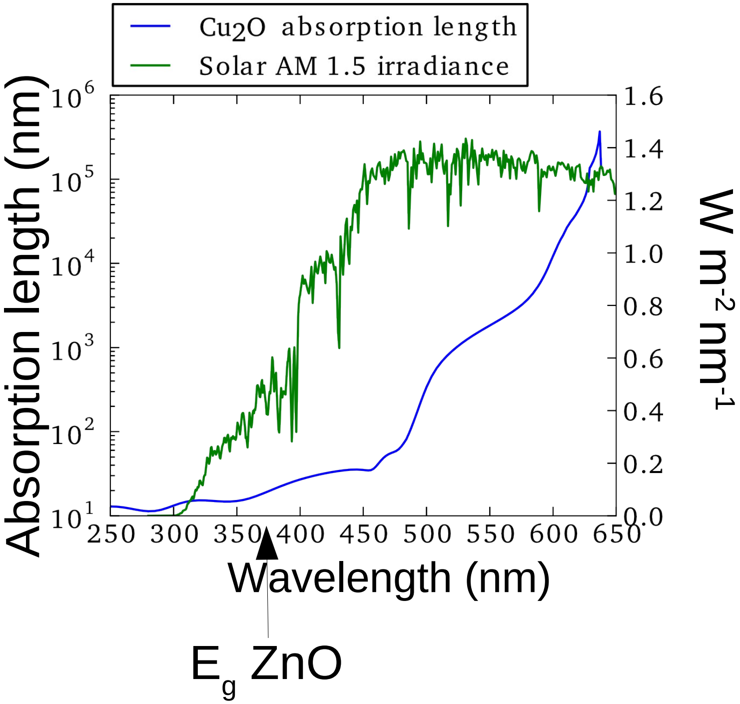




Absorption length derived from data in Malerba, C.; Biccari, F.; Leonor Azanza Ricardo, C.; D’Incau, M.; Scardi, P.; Mittiga, A. Solar Energy Materials and Solar Cells 2011, 95, 2848–2854.

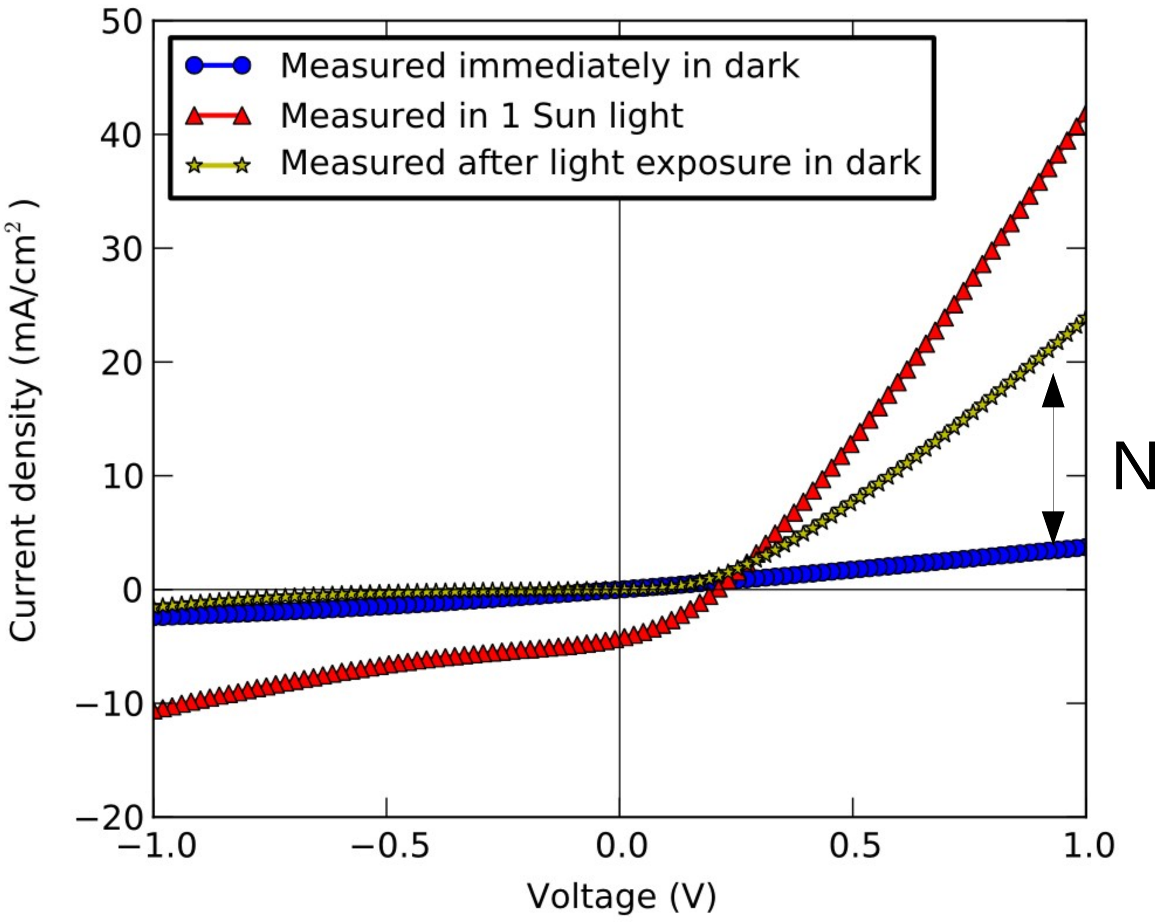
Enhanced carrier collection: EQE





Nanowires increase carrier collection generated by long wavelength photons.

Order of measurements is important

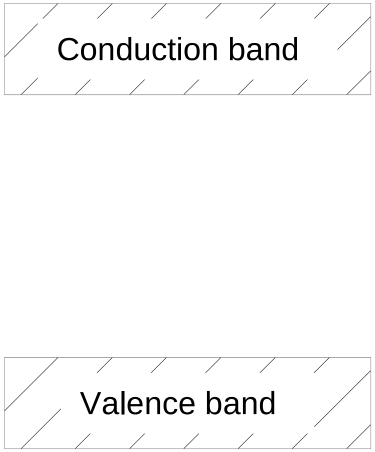


Not the same!

Photoconductivity

$$conductivity = \mu n e$$

μ : mobility
n : electron concentration
e : charge of electron



Photoconductivity

$$conductivity = \mu n e$$

μ : mobility
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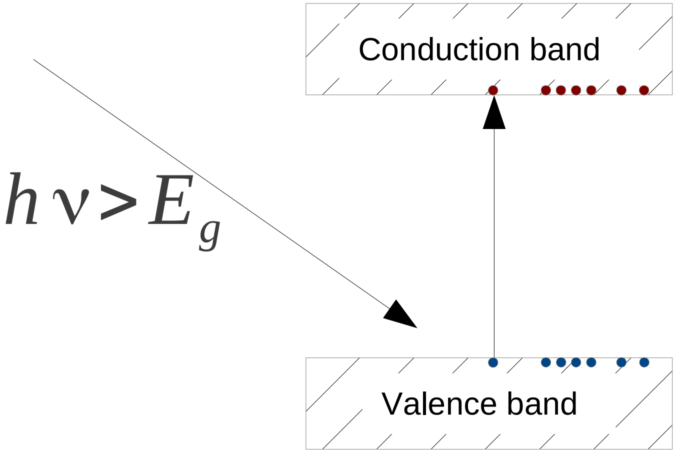
e : charge of electron



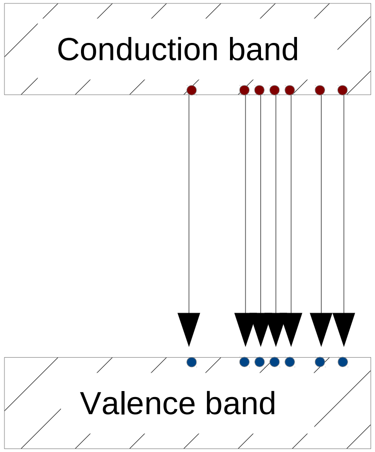
n increases.

Photoconductivity

$$conductivity = \mu n e$$

μ : mobility
n : electron concentration
e : charge of electron

n decreases.

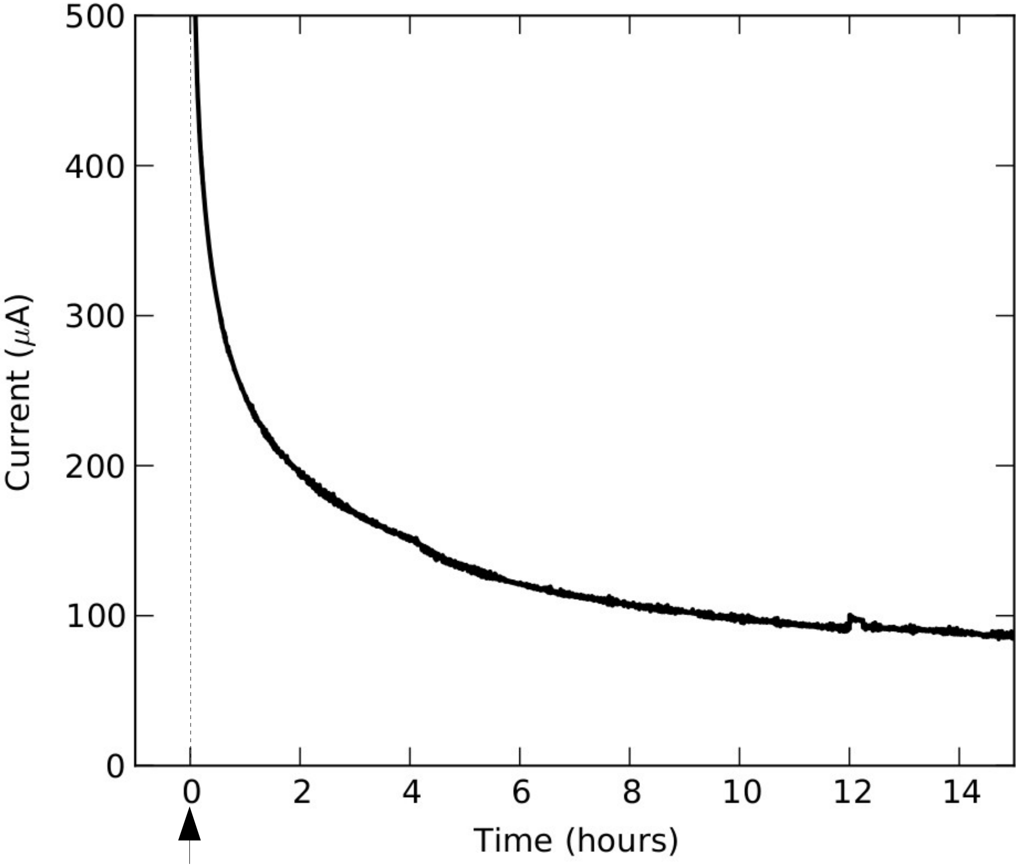


Usually happens ~100 ps for Cu_2O.[1]

---

(1) Paracchino, A.; Brauer, J. C.; Moser, J.-E.; Thimsen, E.; Graetzel, M. J. Phys. Chem. C 2012, 116, 7341–7350.

Decay in conductivity lasts hours



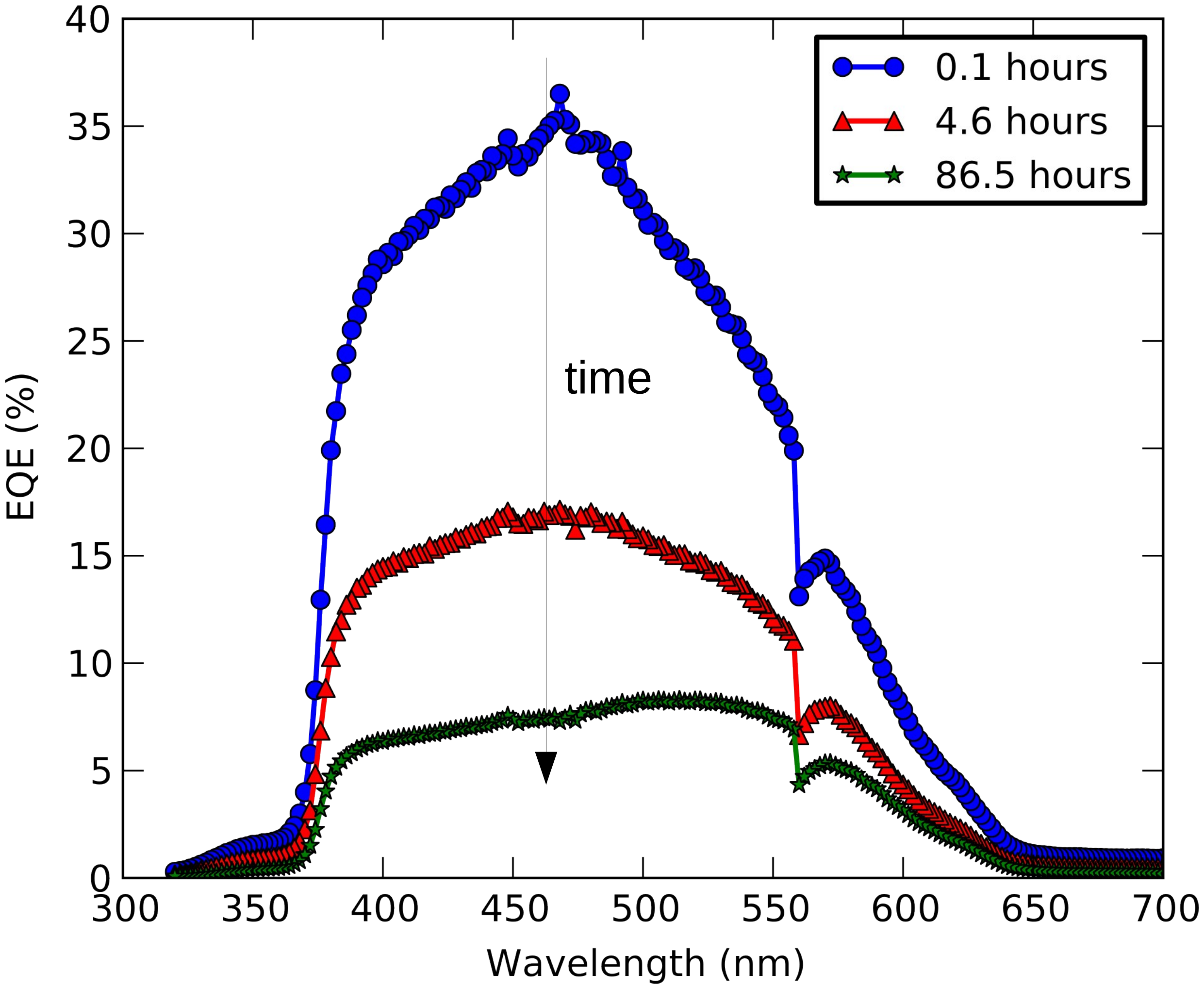
Turned off light at t=0.

EQE decays after initial exposure to light

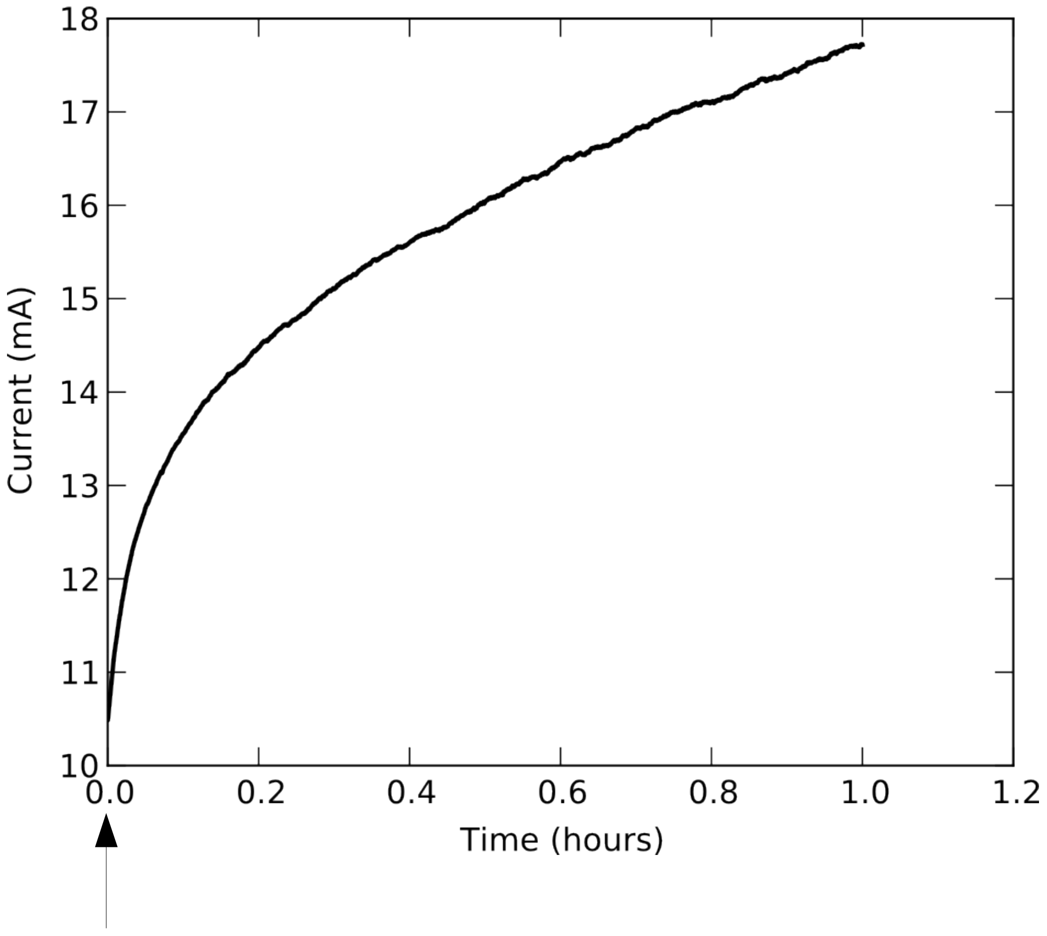
Sample was illuminated with white light.

Illumination stopped at t=0.

EQE decayed after initial illumination.



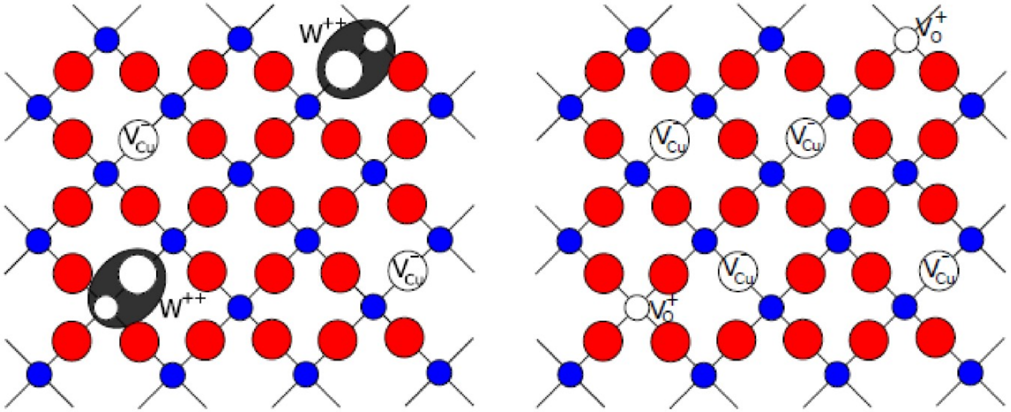
Charging in conductivity is slow



Turned on light at t=0.

Persistent Photoconductivity in Cu_2O

- Semiconductor remains conductive after removal of light – Persistent photoconductivity
- PPC mechanism in Cu_2O is due to dissociation and association of (V_{Cu}-V_O) complexes.



Before illumination After illumination

● Oxygen ○ Oxygen vacancy

● Copper ○ Copper vacancy

In Cu_2O:

$D(V_{Cu}) = 9.6x\ 10^{-10}\ cm^2/s$

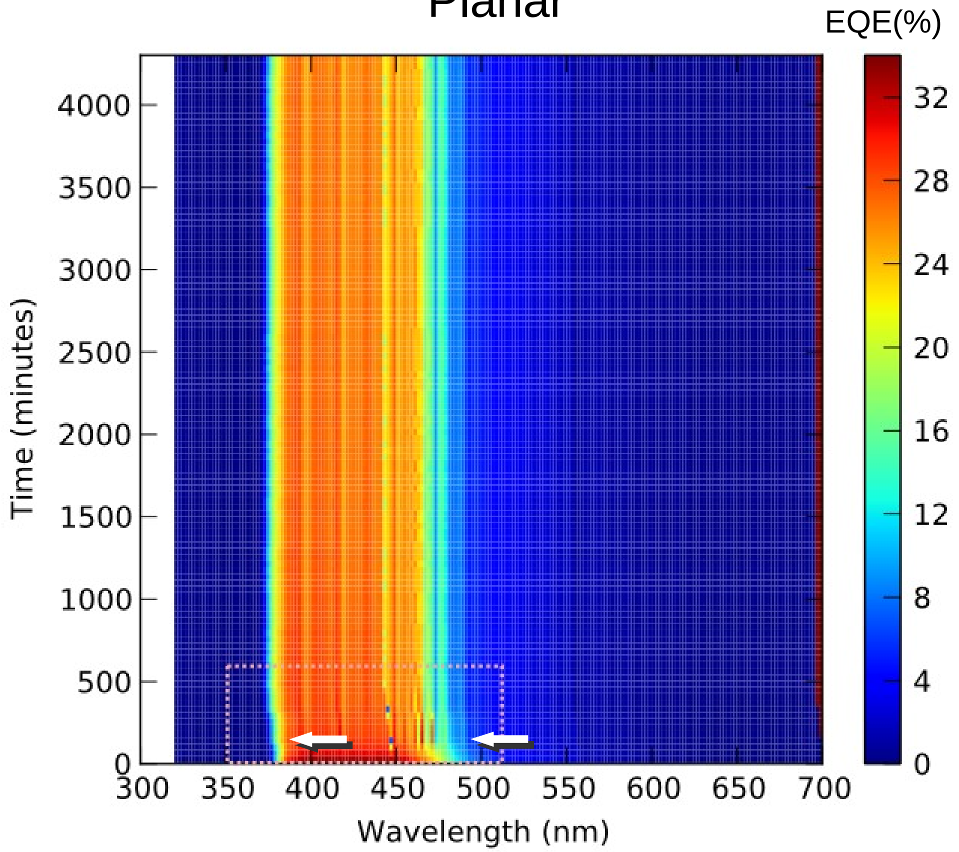
In Si:

$D(B) = 4.6x10^{-54}\ cm^2/s$

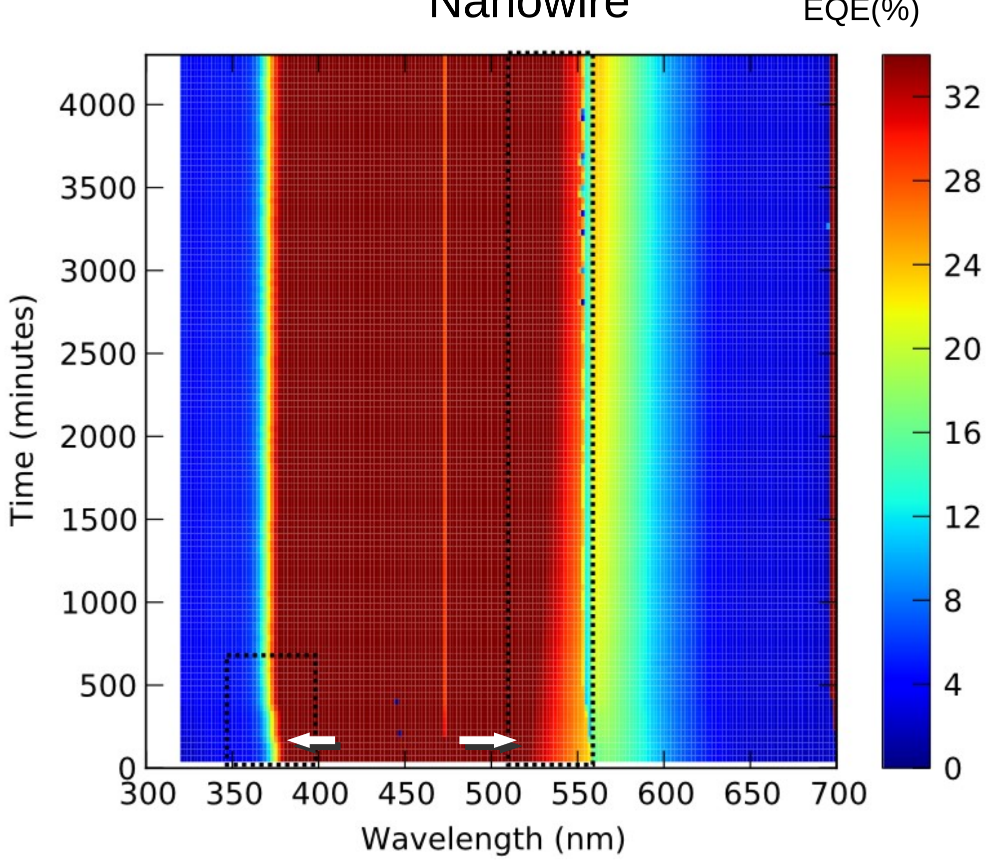
$D(P) = 1.4x10^{-49}\ cm^2/s$

A. Mittiga, F. Biccari, C. Malerba. Thin solid Films, 517:2469, 2009.
J. S. Christensen, H. H. Radamson, A. Y. Kuznetsov, B. G. Svensson, Applied Physics Letters 82, 2254 (2003).

Shifting EQE

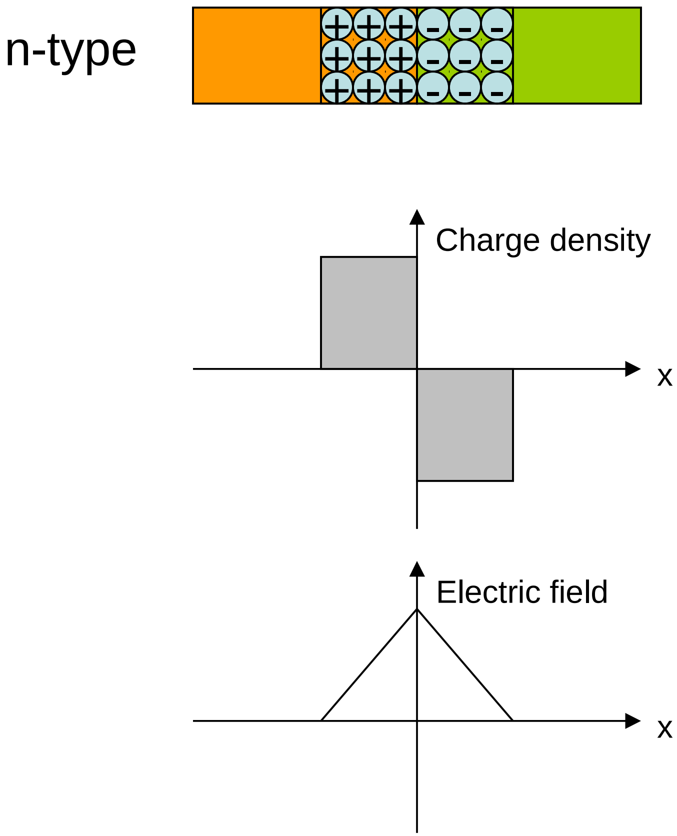


Planar



Nanowire

Mobile V_{Cu} diffuses in Cu_2O



$$\frac{dE}{dx} = \frac{\rho}{\varepsilon}$$

V_{Cu}^{-} are highly mobile compared to other semiconductors.

Internal electric field drives V_{Cu}^{-} motion toward the interface.

In Cu_2O:

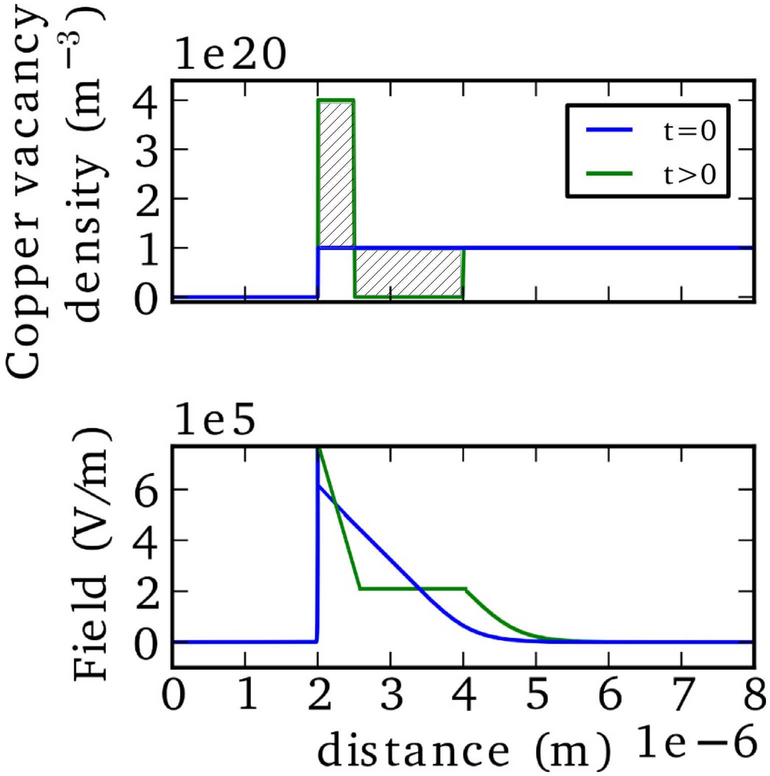
$D(V_{Cu}) = 9.6\text{x } 10^{-10}\ \text{cm}^2/\text{s}$

In Si:

$D(B) = 4.6\text{x}10^{-54}\ \text{cm}^2/\text{s}$

$D(P) = 1.4\text{x}10^{-49}\ \text{cm}^2/\text{s}$

V_{Cu} accumulates at the interface

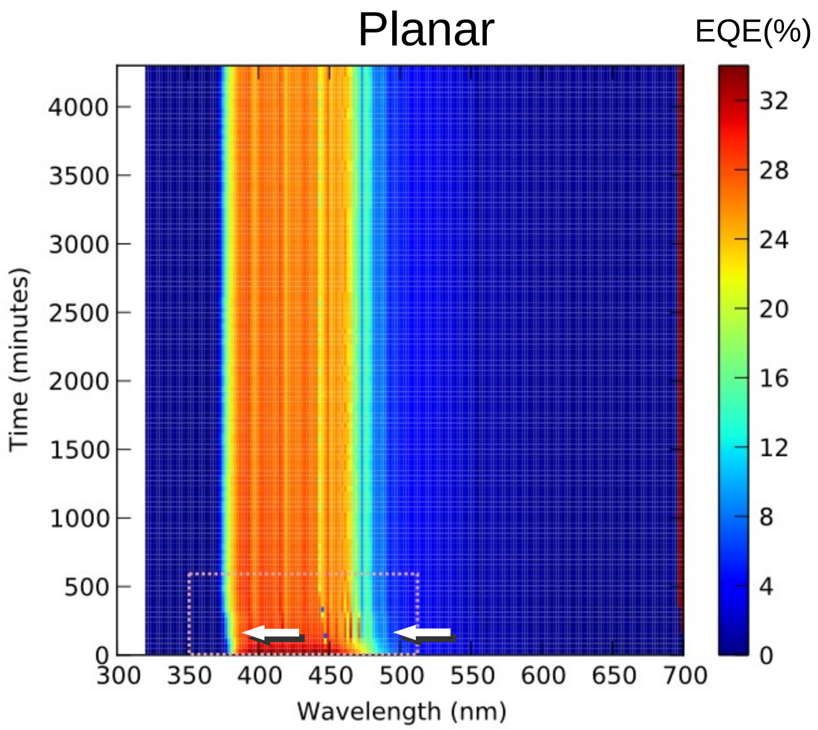


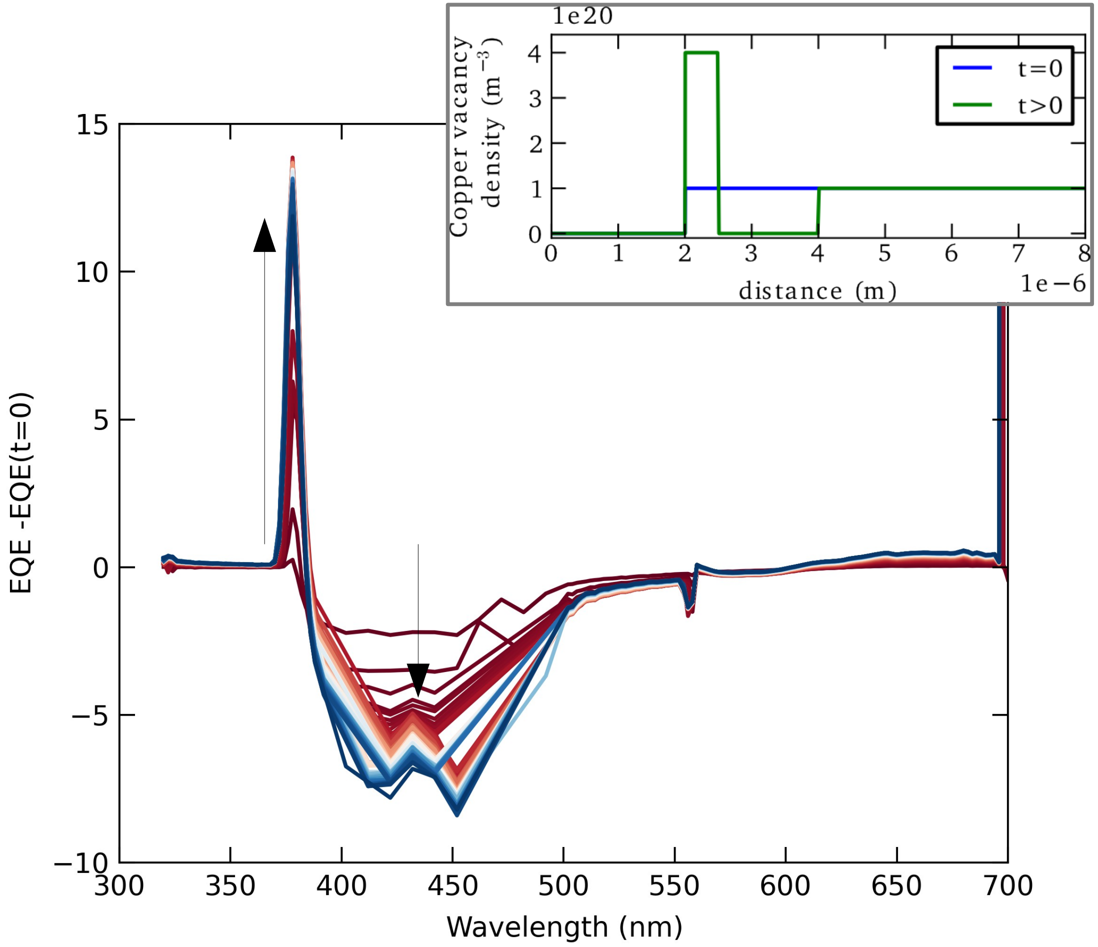
V_{Cu} have moved to the interface, leaving behind a layer depleted of V_{Cu}.

Electric field is larger close the the interface.
is smaller away from the interface.

Carrier collection is better close to the interface.
worse farther from the inteface.

Blue shift in EQE due to accumulation

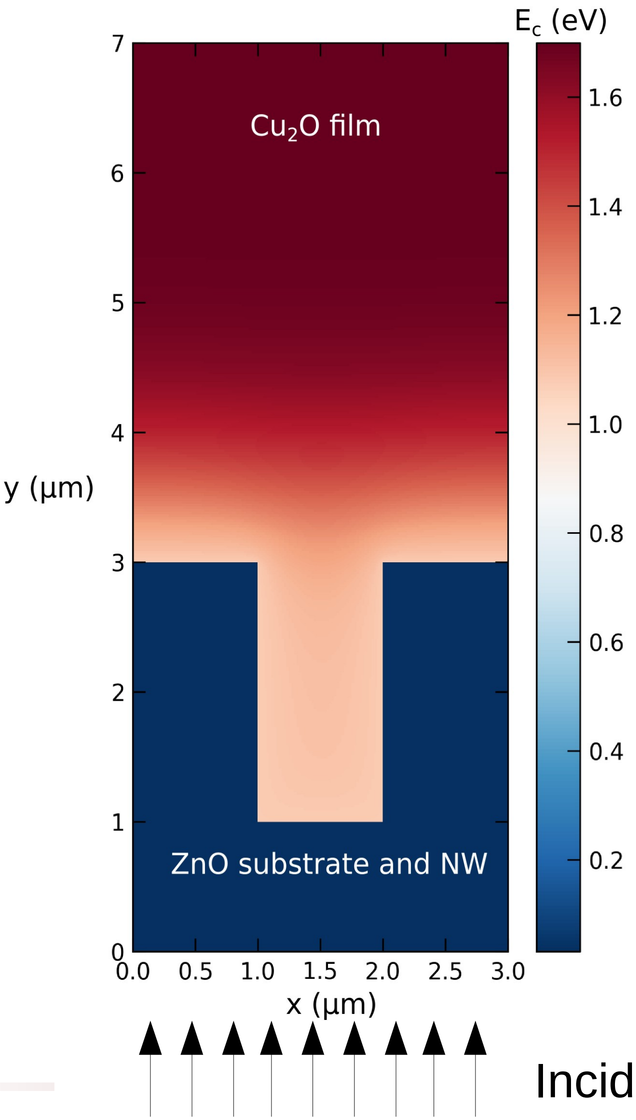




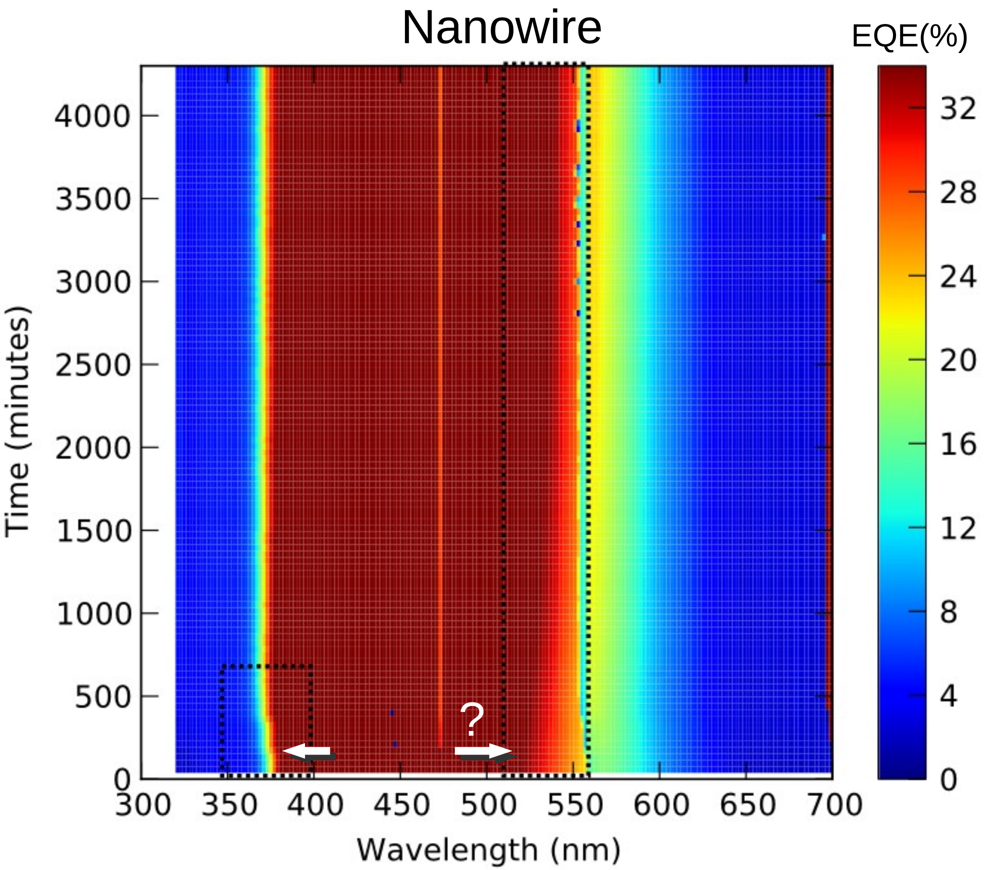
Better collection

Worse collection

Red shift in EQE for NWs due to accumulation

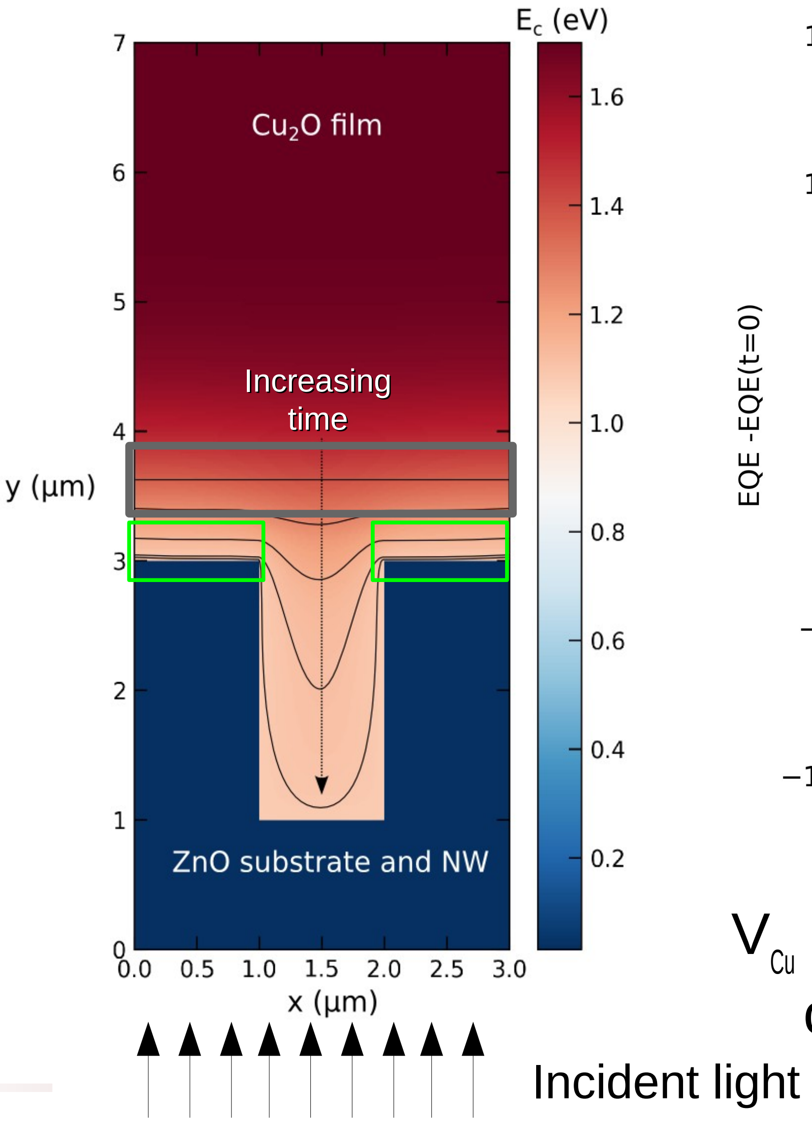


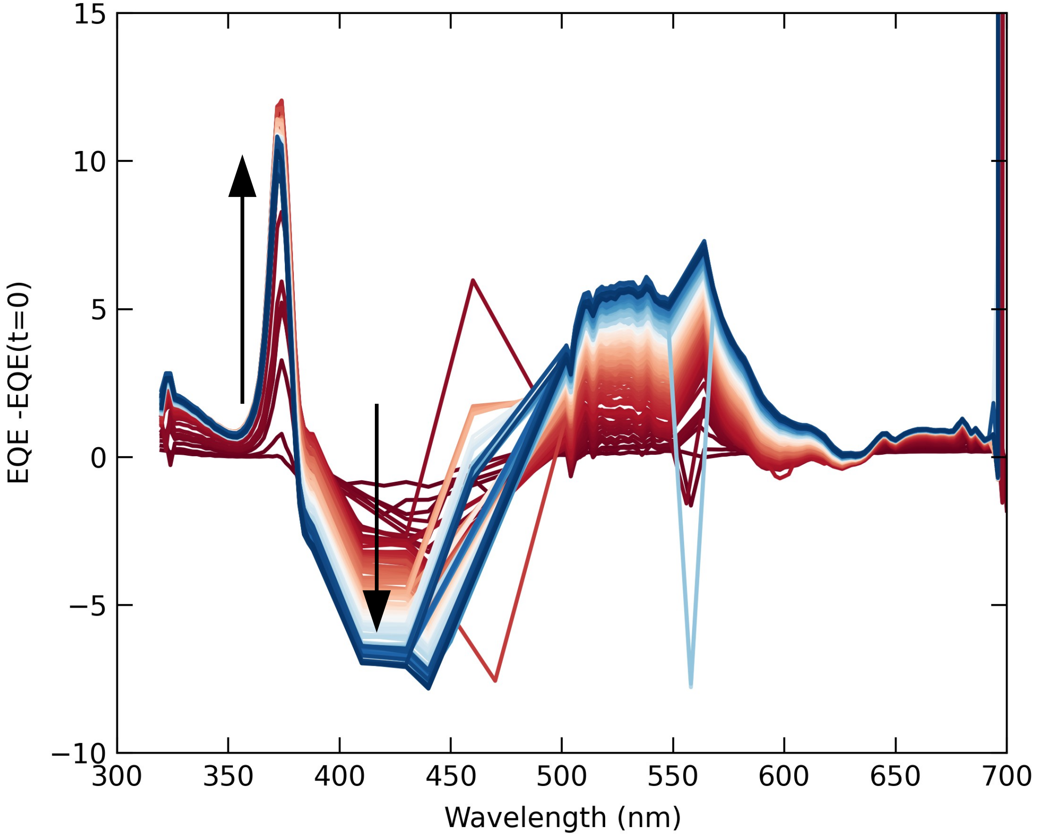
Incident light



Harvard
School of Engineering
and Applied Sciences

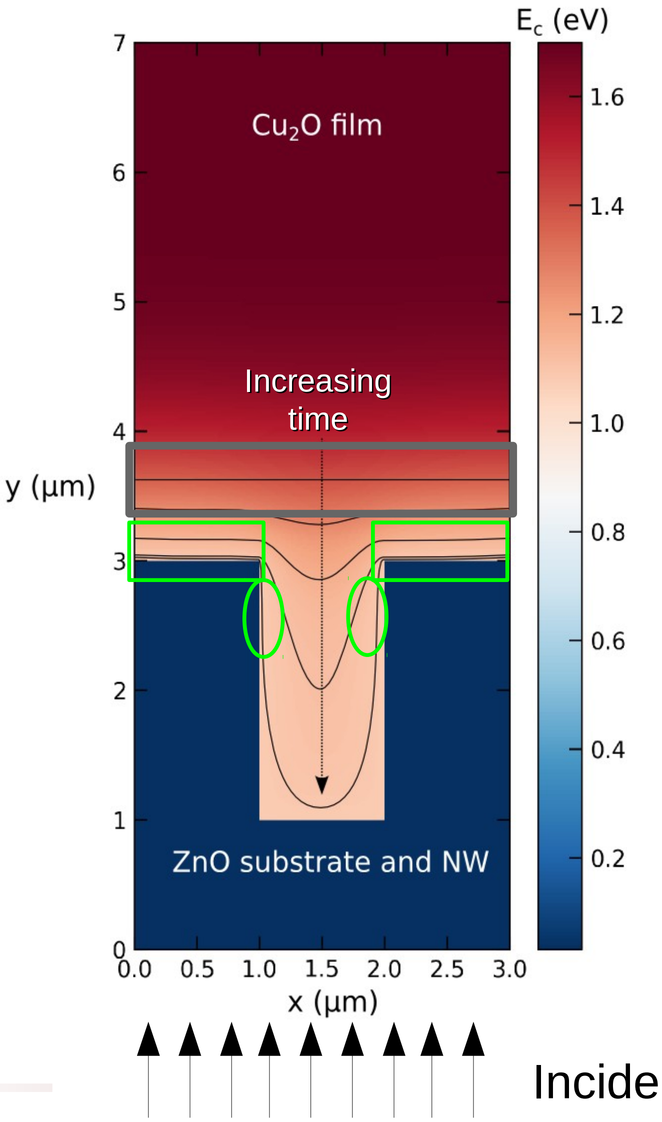
Red shift in EQE for NWs due to accumulation



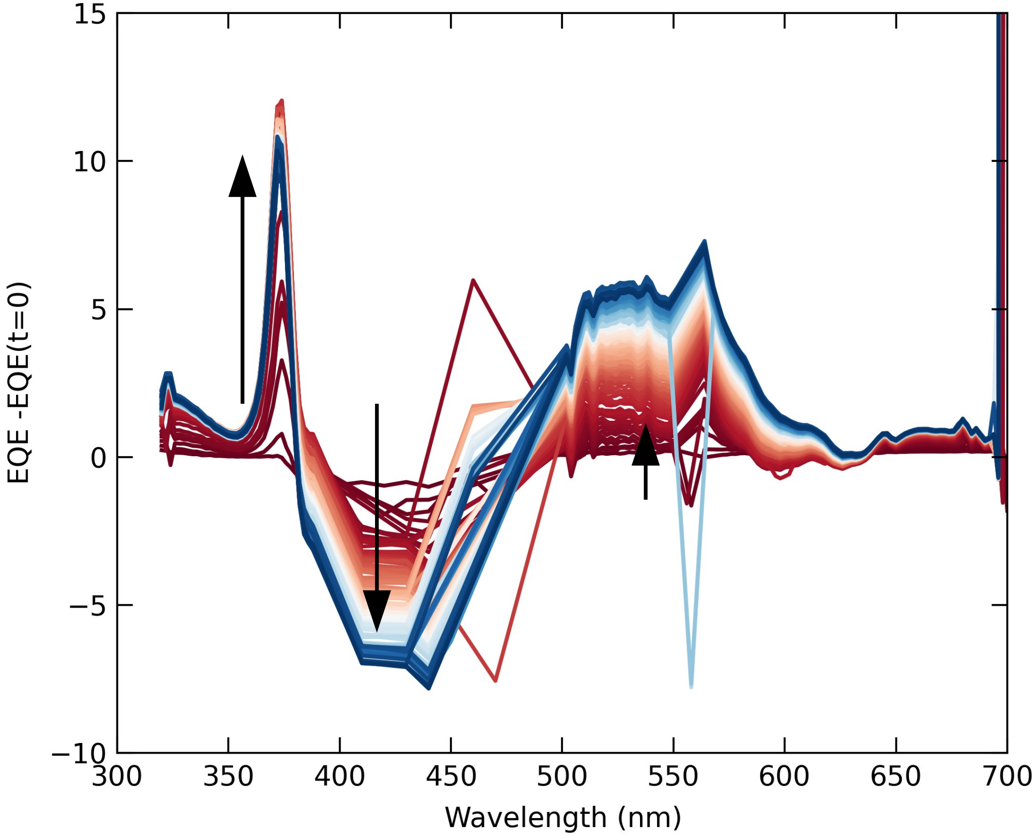


V_{Cu} move into region between nanowires, creating higher electric field regions.

Red shift in EQE for NWs due to accumulation

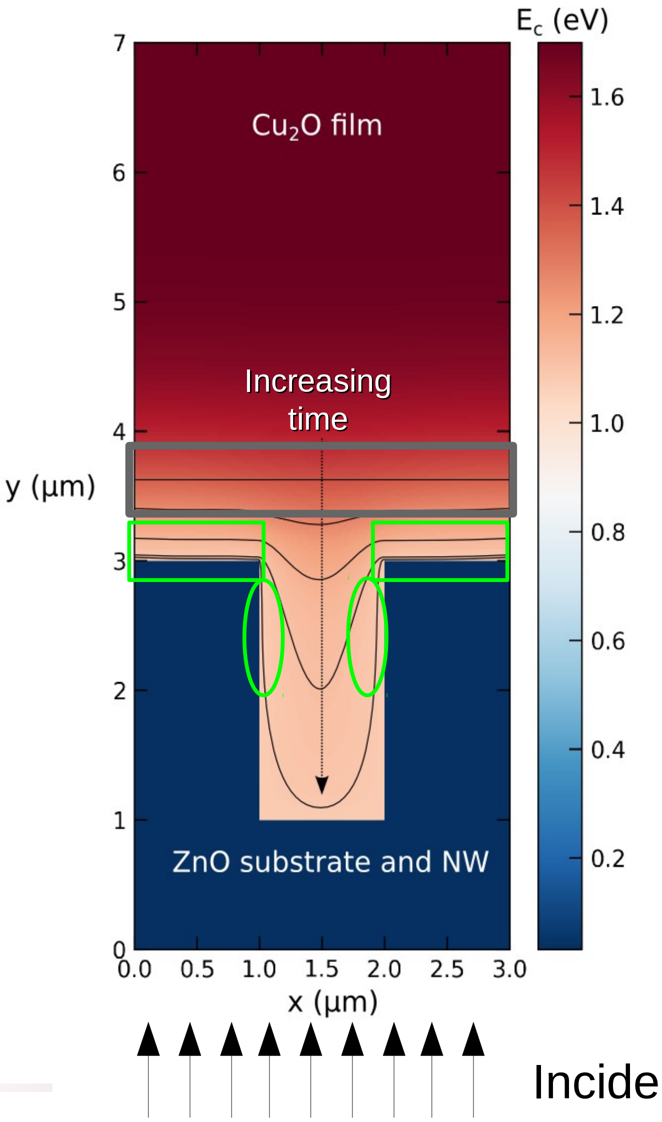


Incident light

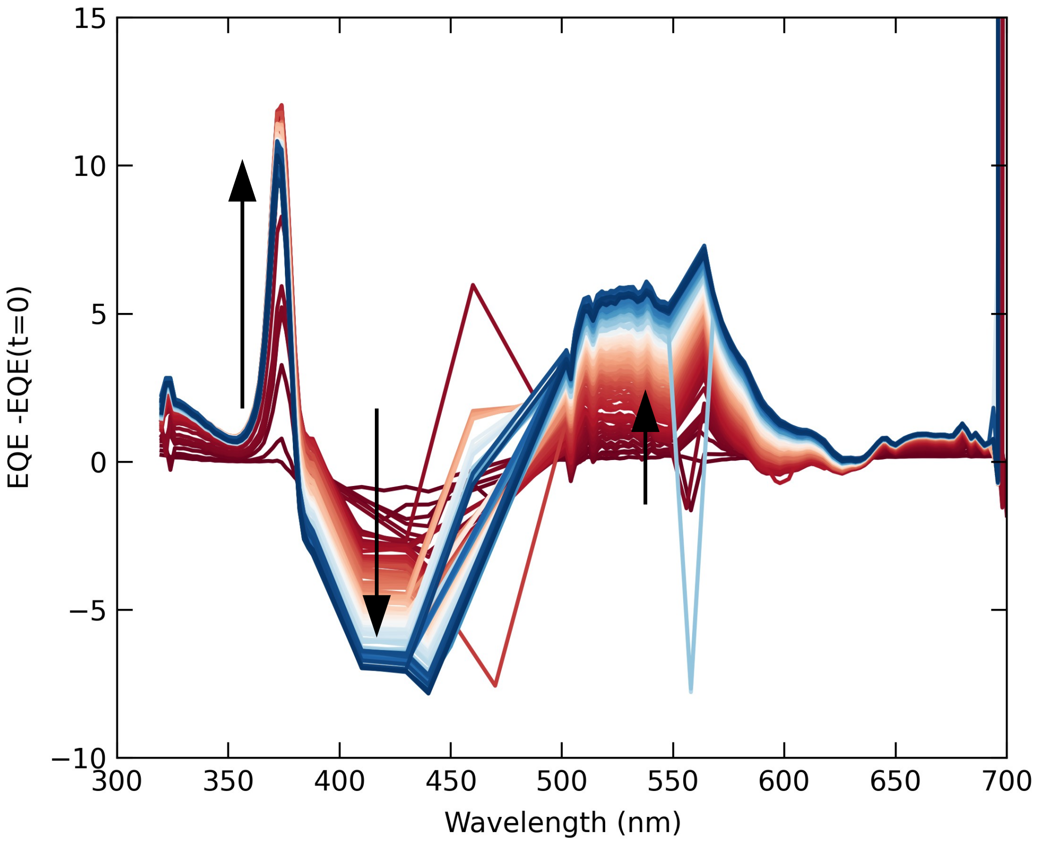


V_{Cu} move into region between nanowires, creating higher electric field regions.

Red shift in EQE for NWs due to accumulation

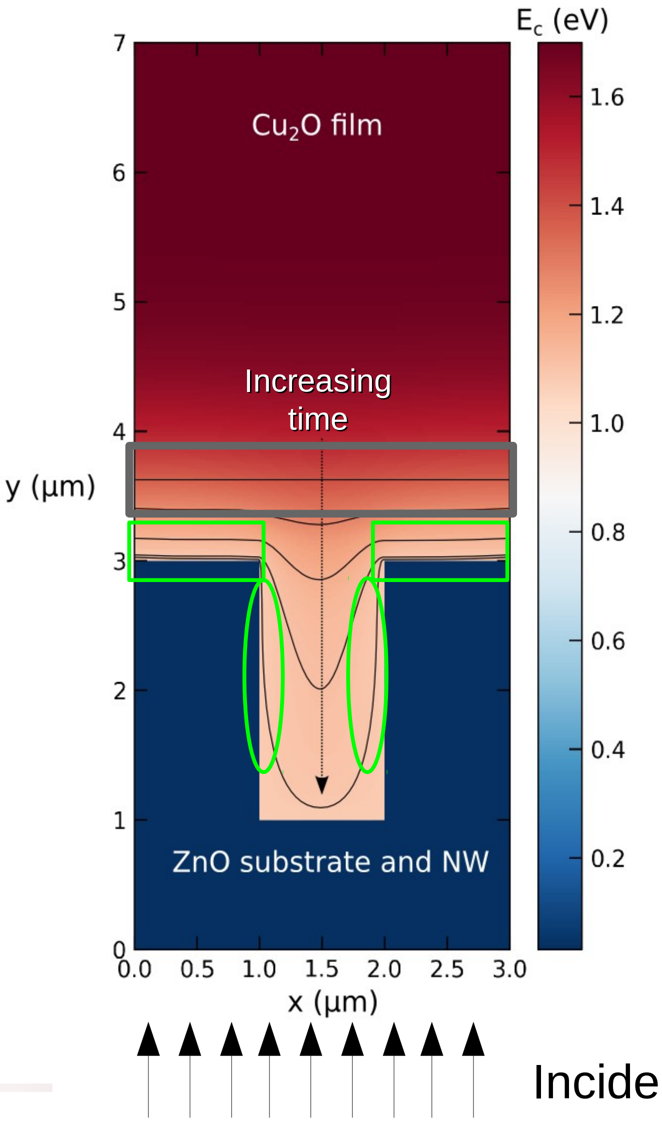


Incident light

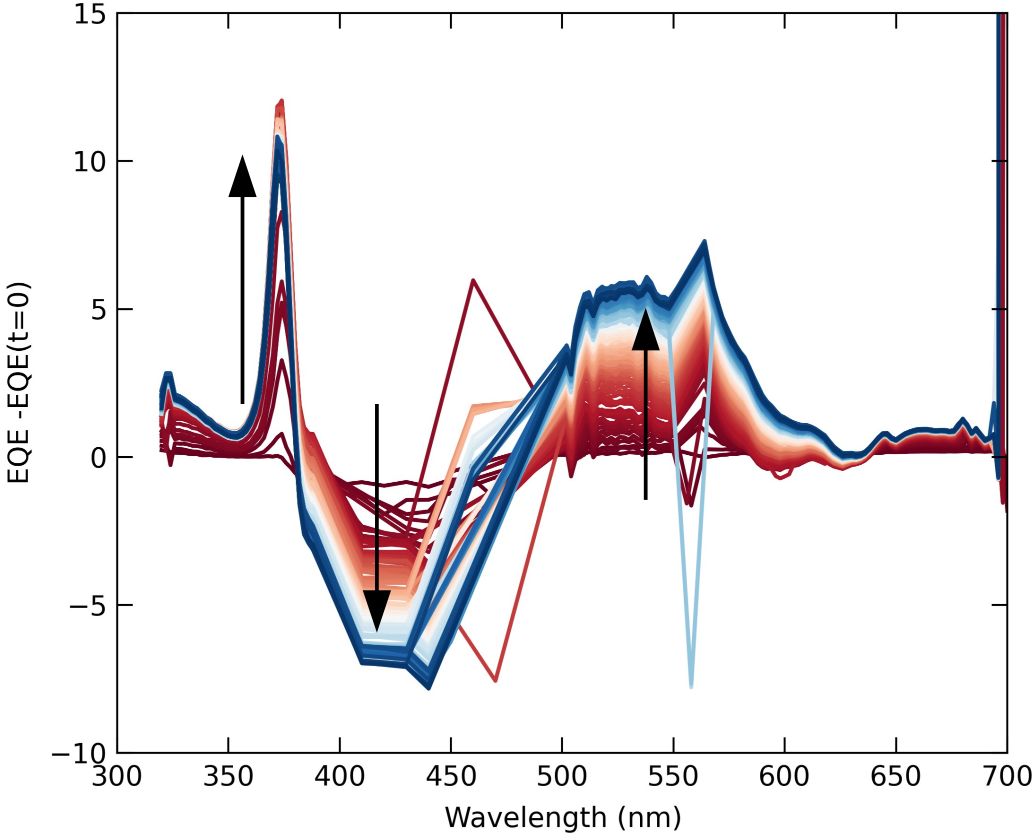


V_{Cu} move into region between nanowires, creating higher electric field regions.

Red shift in EQE for NWs due to accumulation

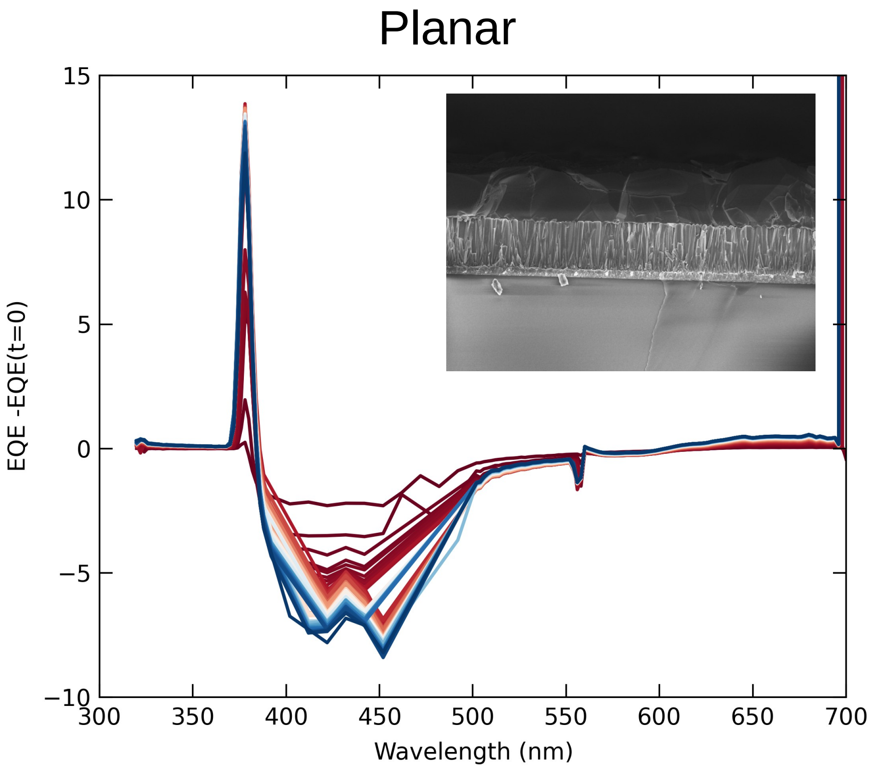


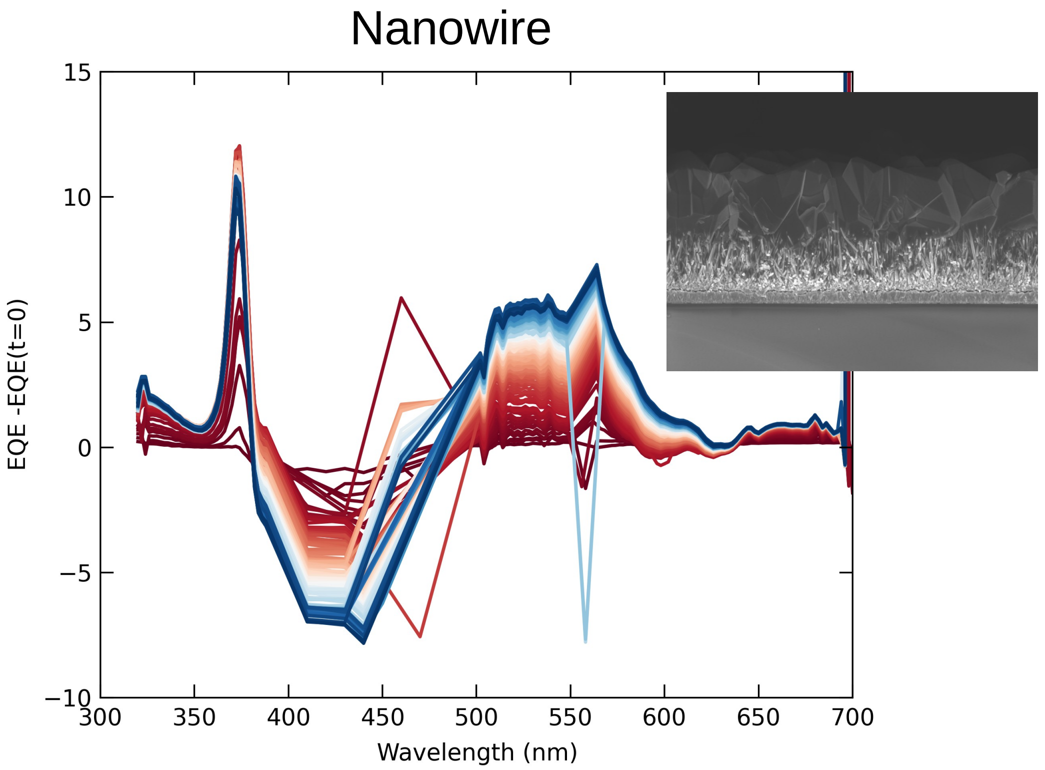
Incident light



V_{Cu} move into region between nanowires, creating higher electric field regions.

Structure changes long term performance





- Long-term changes result from mobile dopant under the influence of the internal electric field.
- Structure of the solar cell can strongly influence the effect and the path of dopant migration.

Summary and Implications

Controlled nanostructure with aqueous ZnO synthesis to obtain both nanowire and planar solar cells

Demonstrated improved carrier collection in the nanowire structure

Observed changes of EQE over time for both planar and nanowire devices, which were explained by moving dopants.

Implications

Nanowire solar cells have potential in increasing carrier collection efficiency.

Long-term testing of solar cells is a critical part of the evaluation process.

Device design must account for possible dopant diffusion, especially in ionic semiconductors.

Creative dopant profiles may be engineered into the structure to enhance device performance.

Thank you for your attention!
Questions?
Acknowledgements to come....

Acknowledgements

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Shawn Mack
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Yinan Zhang

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Antrim

Church communities

Santa Barbara Community Church
Highrock Church

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Alex Woolf
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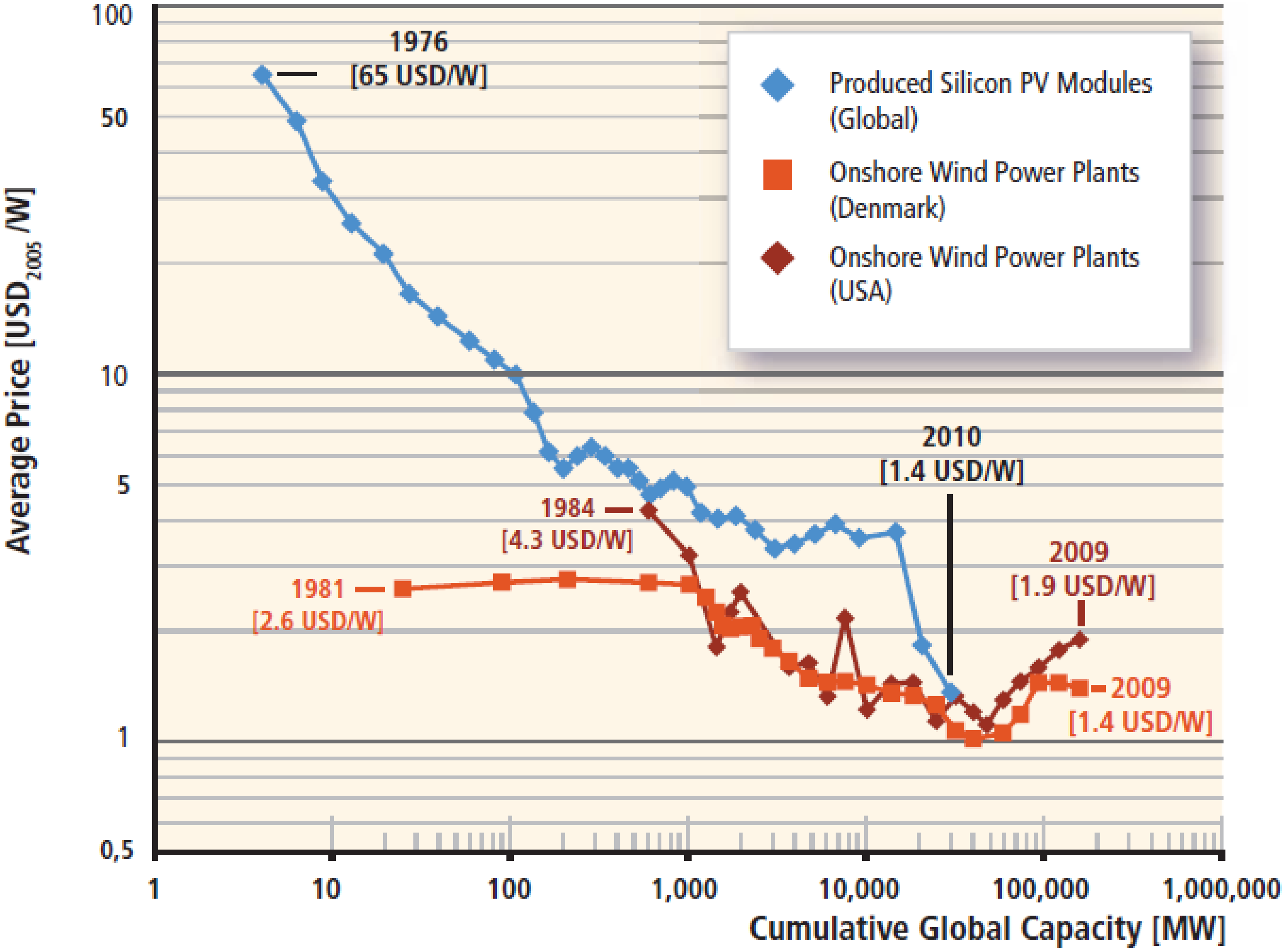
Tina Huang

Danqing Wang
Alex Zhang
Andy Greenspon

Price of wind increased!



In IPCC, 2011: IPCC Special Report on Renewable Energy Sources and Climate Change Mitigation. Cambridge University Press: United Kingdom and New York, NY, USA.

Cu_2O

E_g=2.0 eV

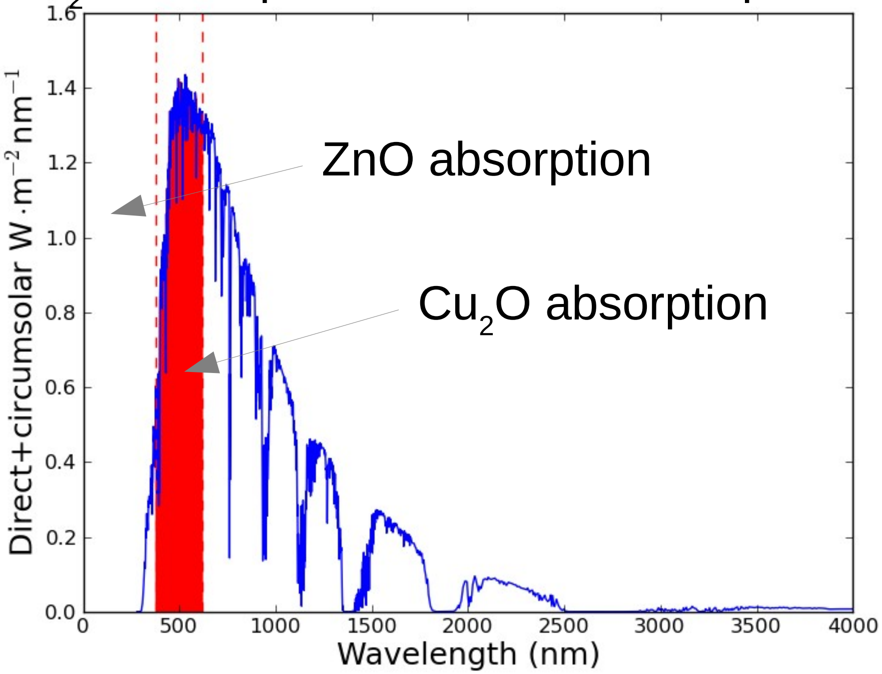
Direct band gap material

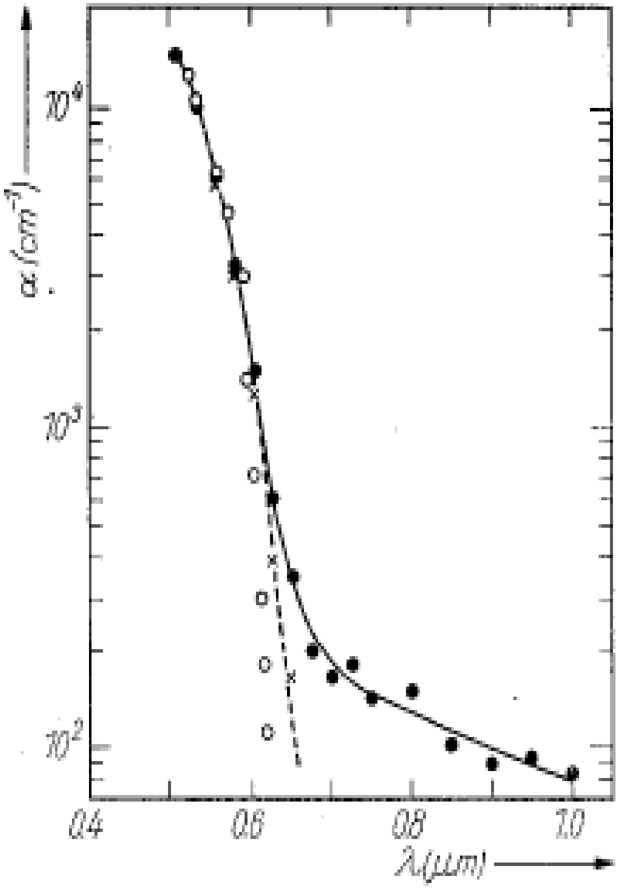
High absorption coefficients (~10^4 cm^{-1})

Typically p-type material, n-type very difficult

Electrodeposition possible for cheap production

Cu_2O Absorption in AM 1.5 Solar spectrum





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1. Olsen, L. C., F. W. Addis & W. Miller (1982) Experimental and theoretical studies of Cu_2O solar cells. *Solar Cells,* 7**,** 247-279.
2. Rakhshani, A. E. & J. Varghese (1987) Optical absorption coefficient and thickness measurement of electrodeposited films of Cu2O**.** *Physica Status Solidi a-Applied Research,* 101**,** 479-486.
3. de Jongh, P. E., D. Vanmaekelbergh & J. J. Kelly (2000) Photoelectrochemistry of electrodeposited Cu_2O. *Journal of the Electrochemical Society,* 147**,** 486-489.

Solar cell circuit analysis

$I = I_L - I_d - I_{sh}$

I = current across load

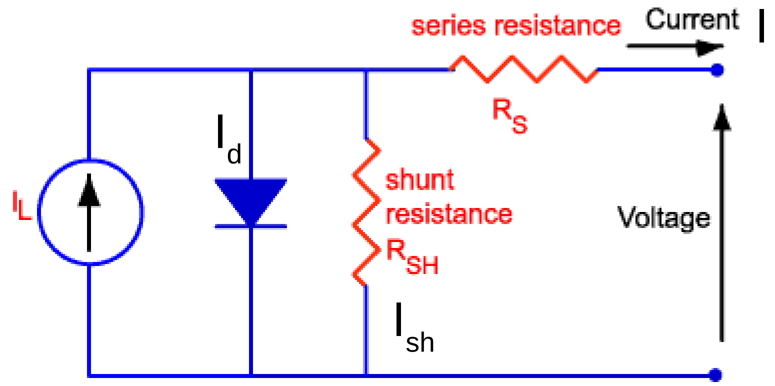
I_d = diode current

I_{sh} = shunt current

$$I_d = I_o\left(\exp\left(\frac{qV_j}{kT}\right) - 1\right)$$

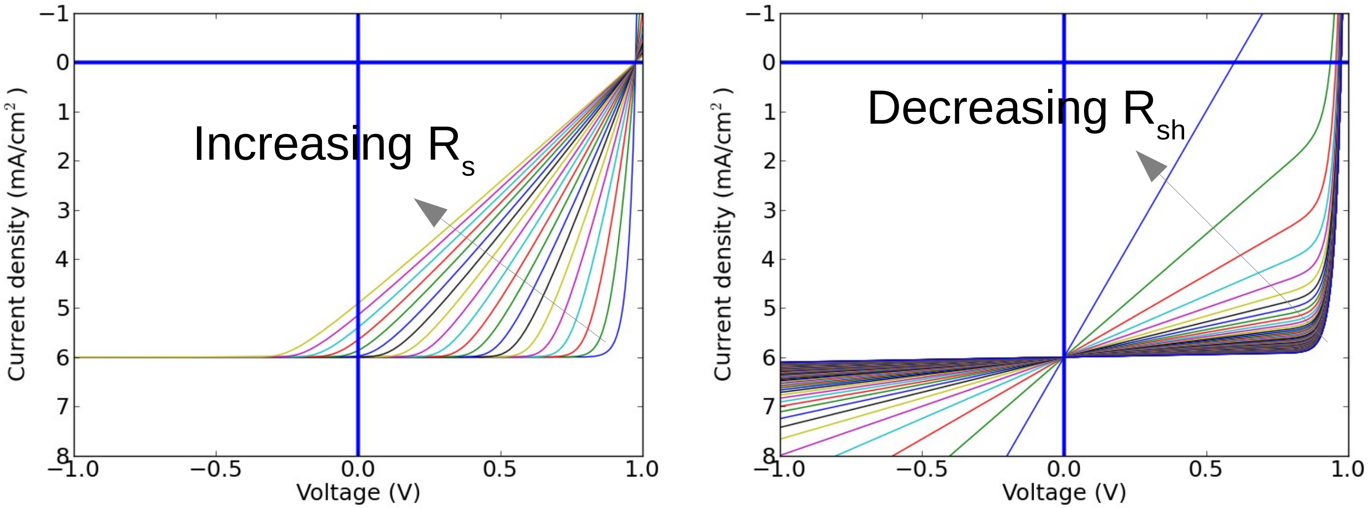
$$I_{sh} = \frac{V_j}{R_{sh}}$$

$$V_j = V + IR_s$$

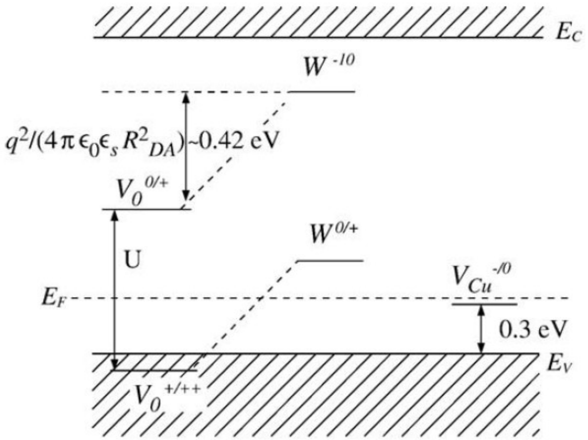


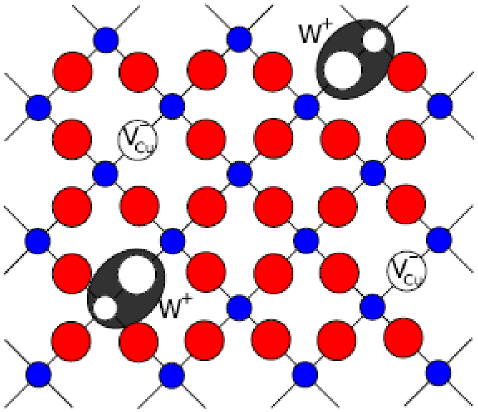
Shunt and series resistance modeled in solar cell circuit.[1]

Effect of R_s and R_{sh} on Solar Cell JV curves

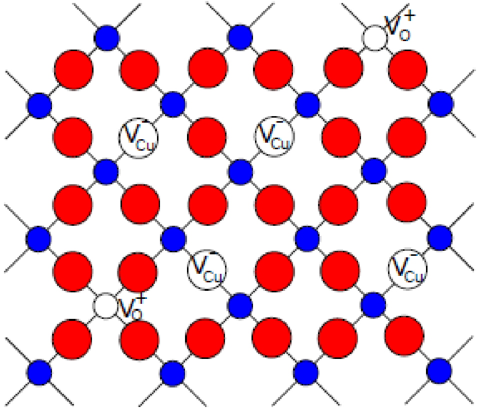


PPC (complexing model)





Before illumination



After illumination

Before illumination:

$$V_{Cu}^- — V_O^+ \longrightarrow W^0 \text{ (unstable)} \longrightarrow V_{Cu}^- — V_O^+$$

$$V_{Cu}^- — V_O^{++} \longrightarrow W^+ \text{ (stable)}$$

During illumination:

$$W^+ + e^- \longrightarrow W^0 \longrightarrow V_{Cu}^- + V_O^+$$

Illumination is stopped:

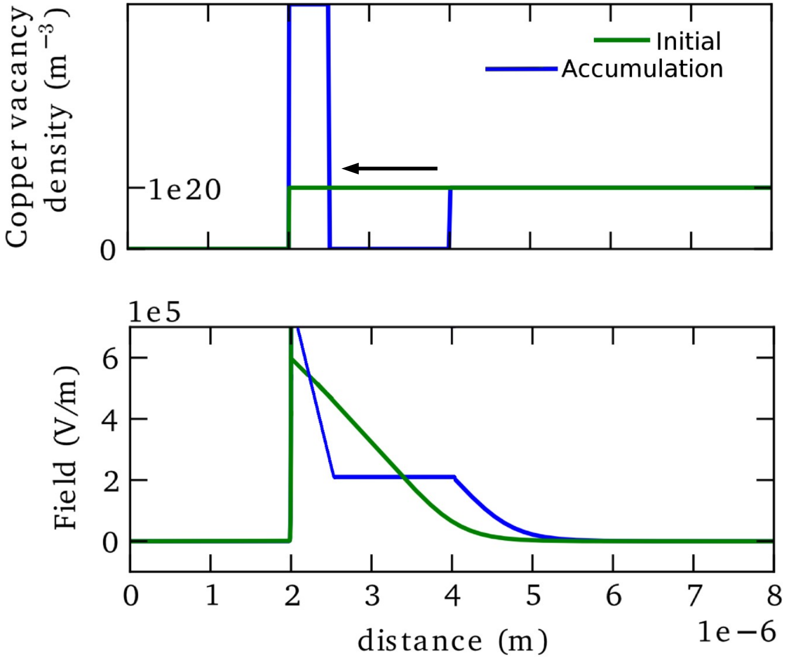
V_O^+ cannot be restored to V_O^{++} through hole capture, because V_O^+ energy level is above Fermi level.

V_{cu}^- must diffuse back to V_O^+ to make W^0, which can capture a hole to become W^+.

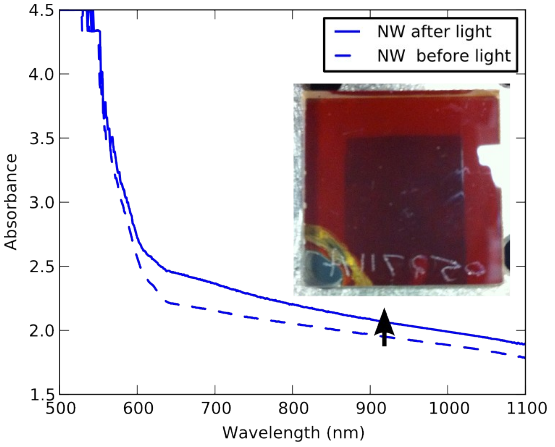
Passivation of V_{Cu}^{-} at interface

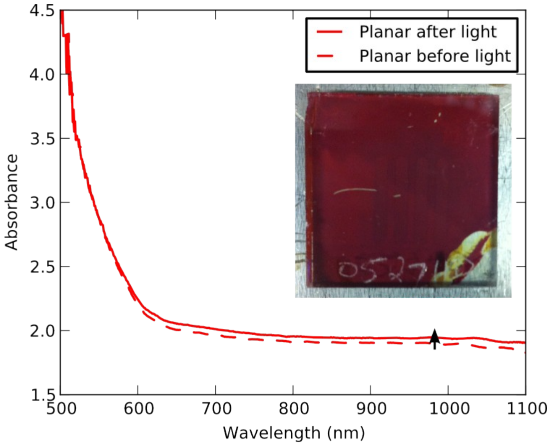
H^+ from ZnO complexes with V_{Cu}^{-}

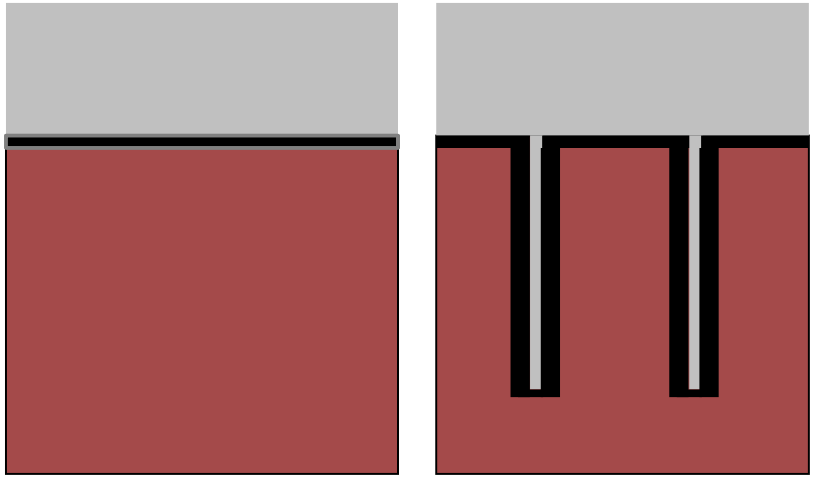
V_{Cu}^{-} oxidizing to V_{Cu}^{2-} and forming CuO at interface



Cu_2O darkens after long exposures to light







Difference in absorbance