Photon Enhanced Thermionic Emission

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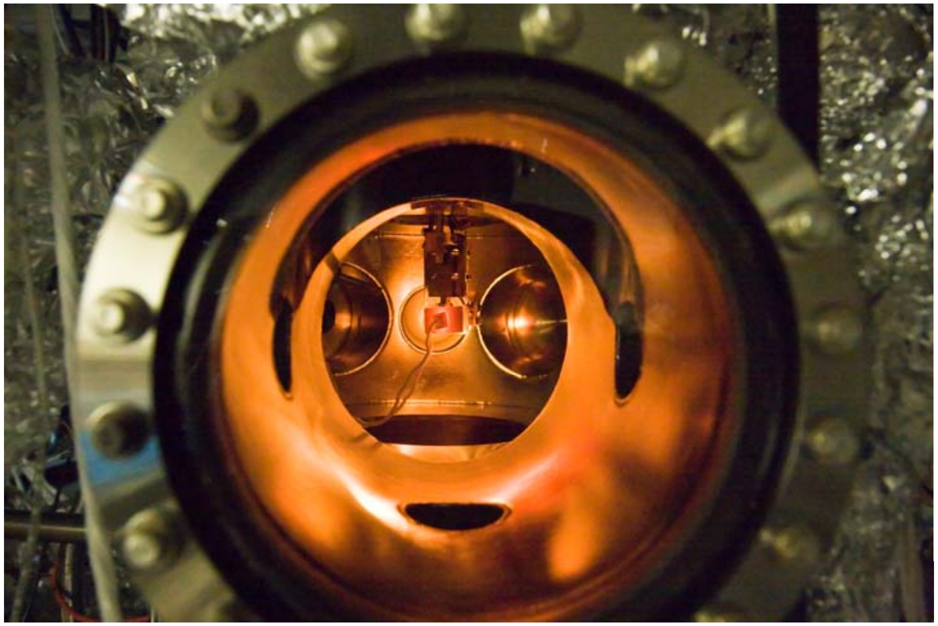

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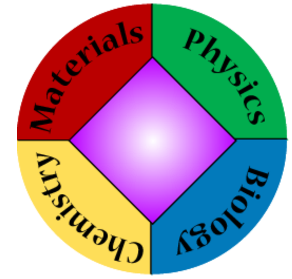
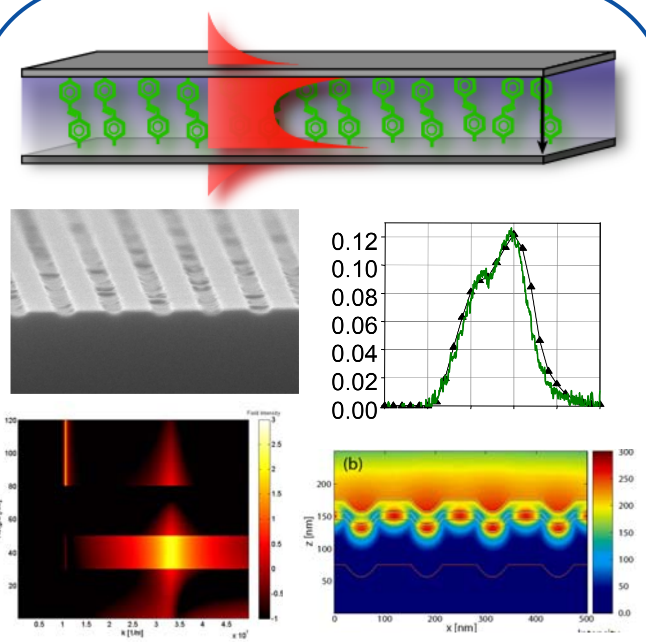
The Melosh Group

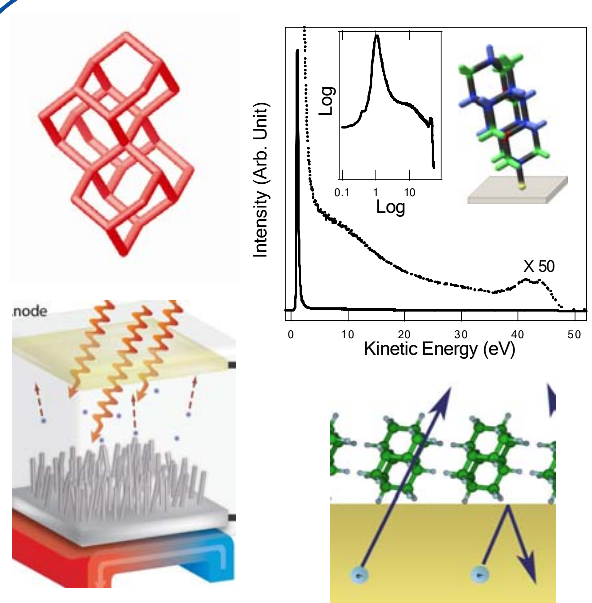


Nanomaterials Behavior at Interfaces

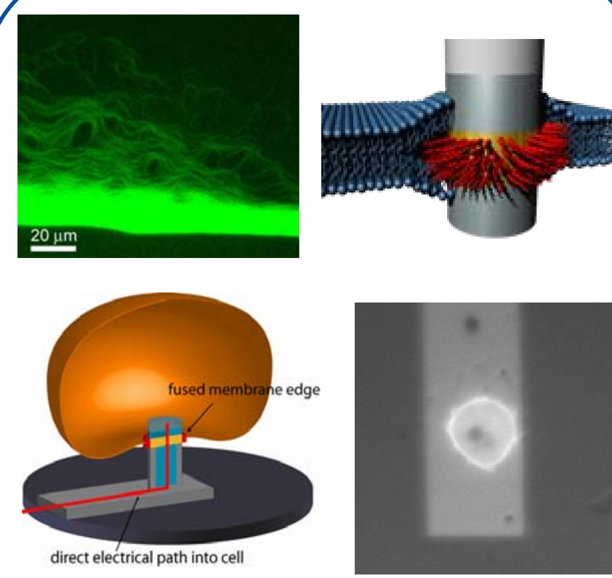
- Fabricating, interrogating, and controlling nanoscale materials at interfaces
- Applications for Energy, Biology, and Electronics



Molecular Plasmonics



Diamondoids and Energy

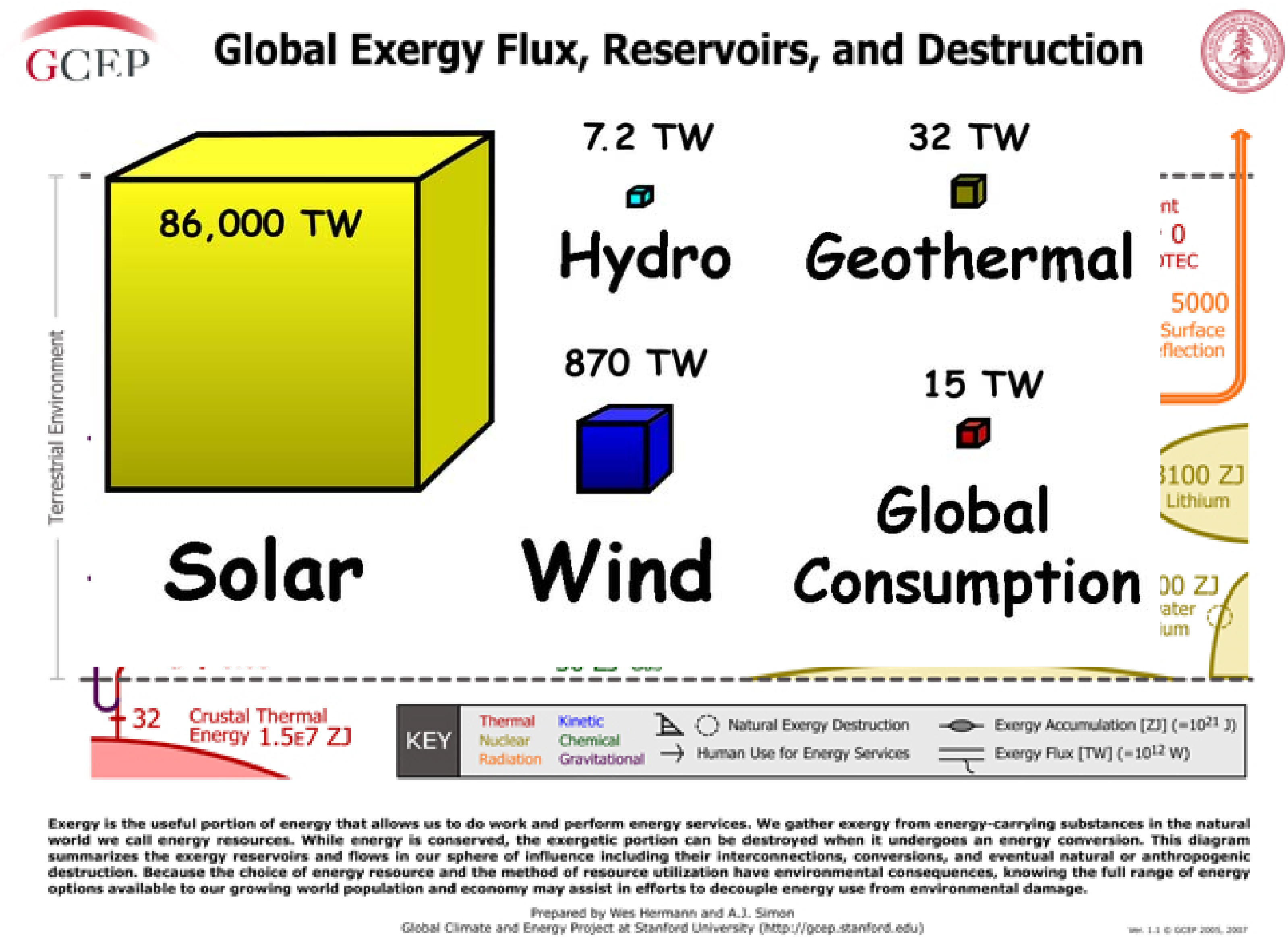


Bio-Electronic Interfaces

Today's Overview

1. *Solar harvesting methods*
2. *How can we dramatically increase efficiency?*
3. *The PETE process*
4. *Improving PETE performance*

Solar Energy is going to be Important



wikipedia; data from Energy Information Administration

Solar Power Conversion

A lot of high-quality energy is available from the sun… how can we harvest it?

Solar Thermal

- **Converts sunlight into heat**
- **Uses well-known thermal conversion systems**
- **Efficiencies of 20-30%**

Photovoltaics

- **collects fraction of incident energy**
- **“high grade” photon energy**
- **direct photon to electricity**
- **efficiencies 19-24% (single junction Si)**

Photovoltaics

Thin Film

Thin layers of Si, CdTe, CIS are cheaply coated onto large area substrates. Lower performance but also lower cost than monocrystalline Si. Typical efficiencies vary according to materials; CIGS ~20%; CdTe ~14%, α-Si ~4-8%.

Companies: First Solar (CdTe), United Solar (a-Si), Sharp

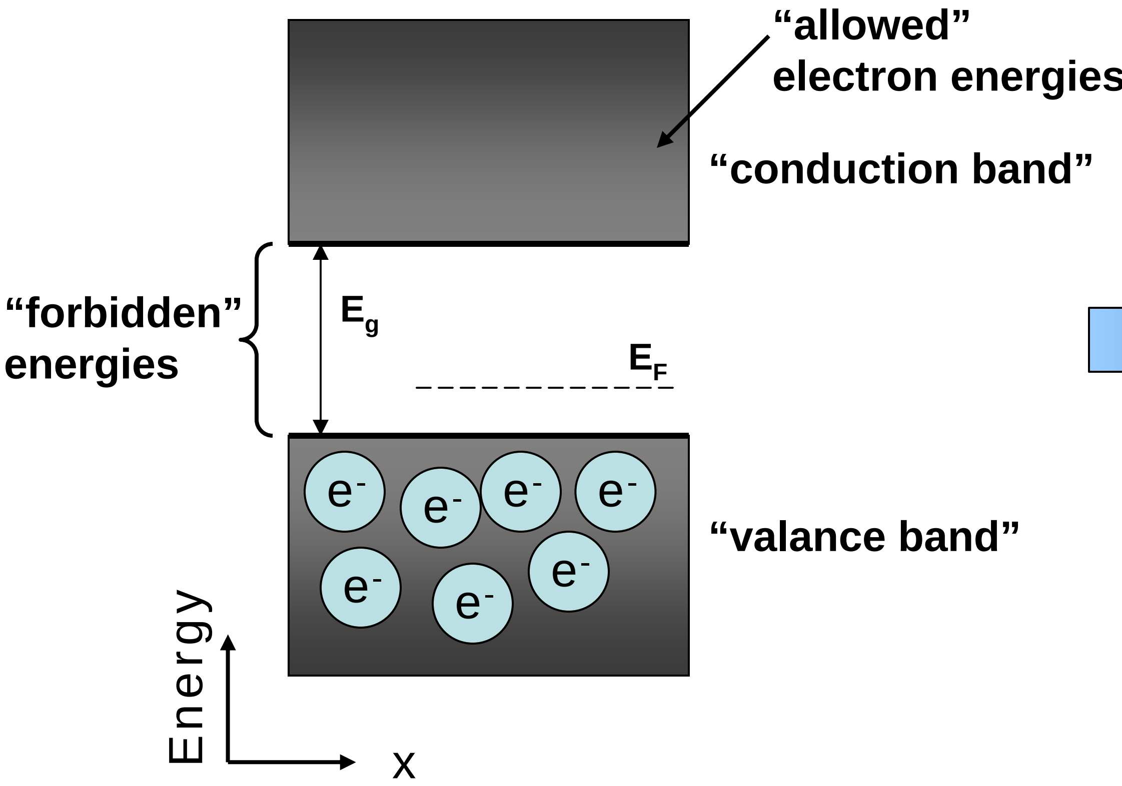
Mono/ Multi crystalline Silicon

Thick wafers of highly pure, single crystalline Si are mounted on a flat panel. High quality, but more expensive than thin films. Typical efficiencies 14-21% range

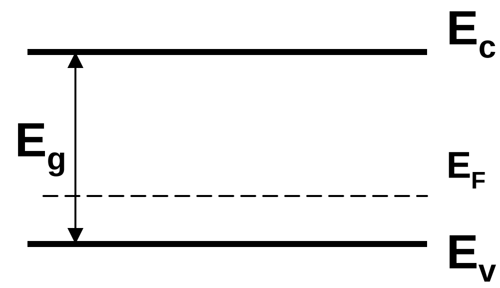
Companies: Sun Power, Yingli, Q-cells, Suntech, Sharp

Semiconductor Materials

Energy Level Diagrams

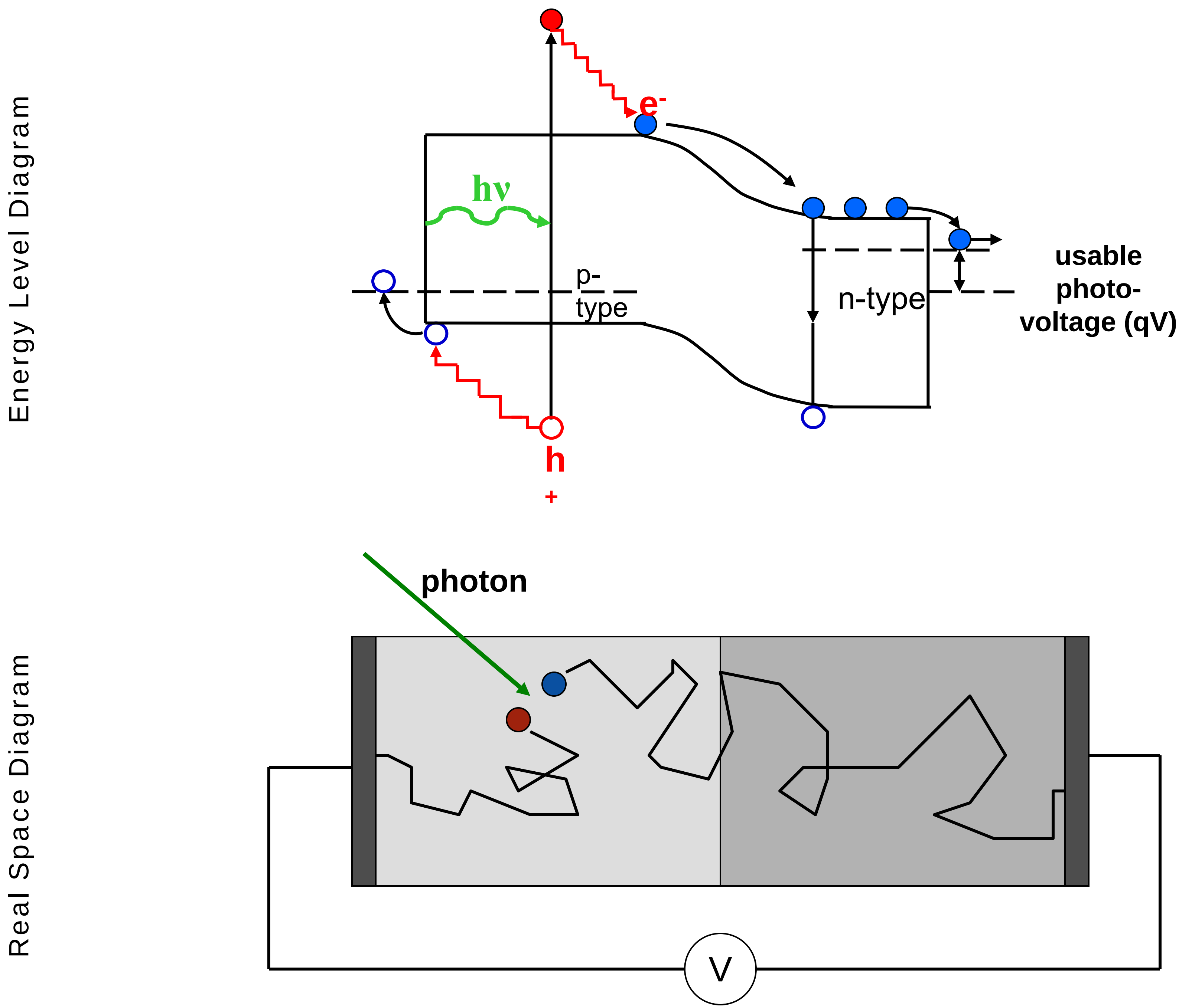


Simplified Energy Level Diagram

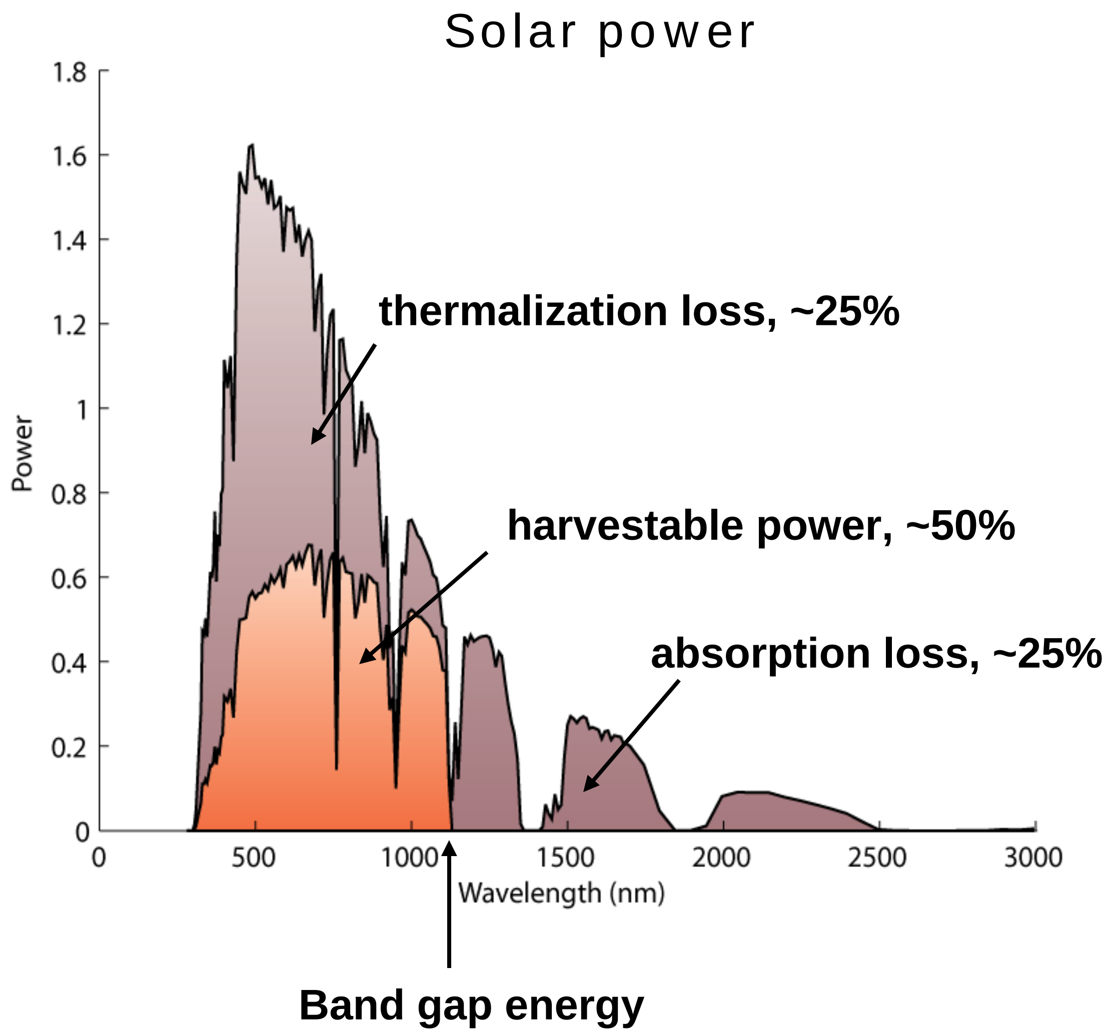


Silicon

Photovoltaic Operation



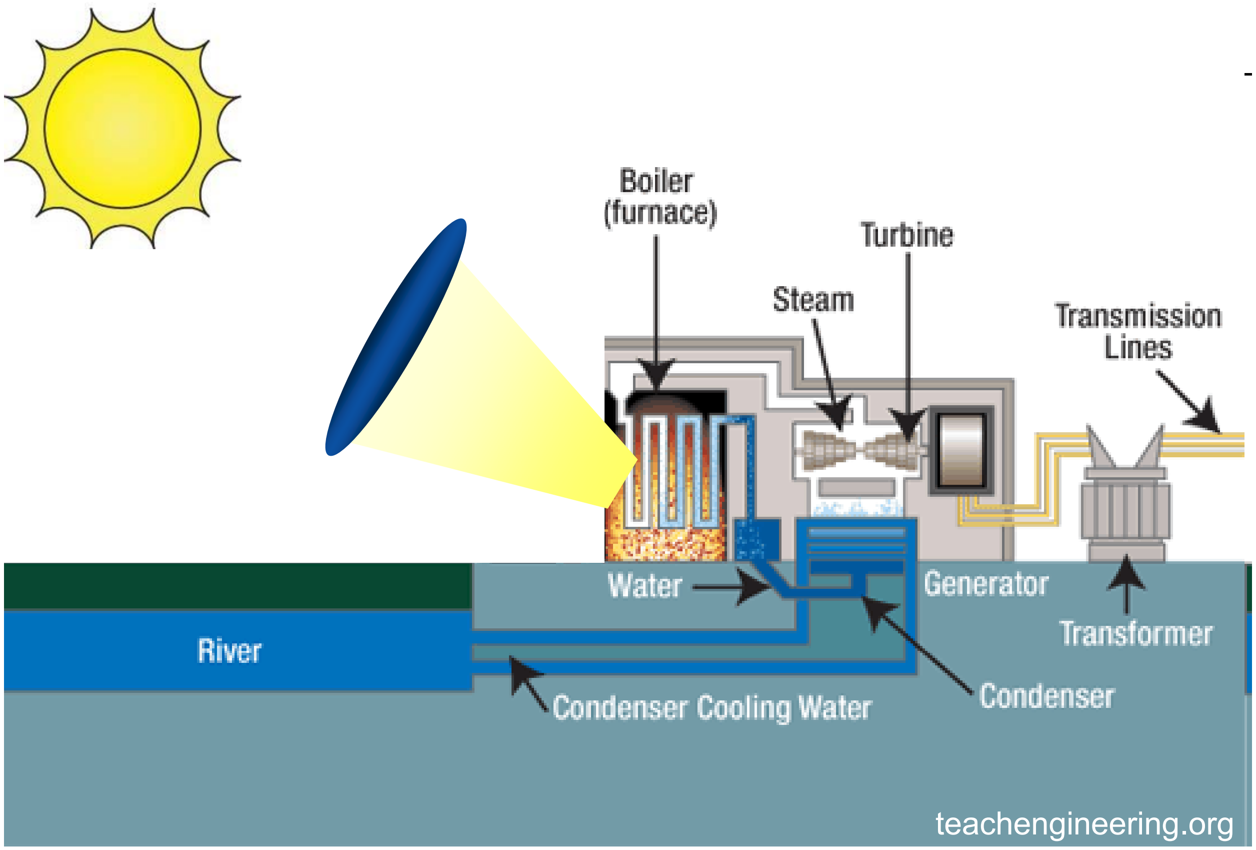
Issue with single-junction PV's



- Lose ~50% of incident energy immediately
- Given off as heat
- Further fundamental limits reduce maximum possible efficiency to ~34%
- Monocystalline Si collects almost all the electrons created

Thermal Conversion

Solar conversion plant:



Solar Thermal Conversion

Power Tower

Flat panel reflectors focusing onto single tower. Conventional steam/liquid salt operation.

Companies: Brightsource, Abengoa, eSolar

Parabolic Dish/ Stirling Engine

Dishes focus light onto individual thermal engine, such as a Stirling engine.
Companies: Tessera Solar,

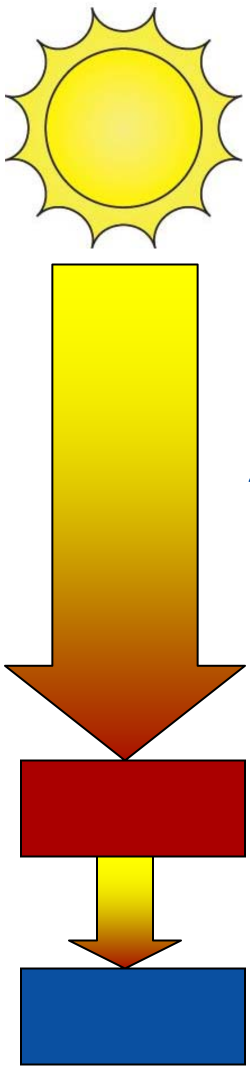
Parabolic Troughs/ Fresnel reflectors

Trough reflectors focusing light onto pipe, heating working fluid, which heats water for standard steam cycle.

Companies: Ausra, Siemens, Solar Millennium

A simplistic comparison

Thermal Collectors



5800º C

ΔT = 5200º; *un-used*

600º C

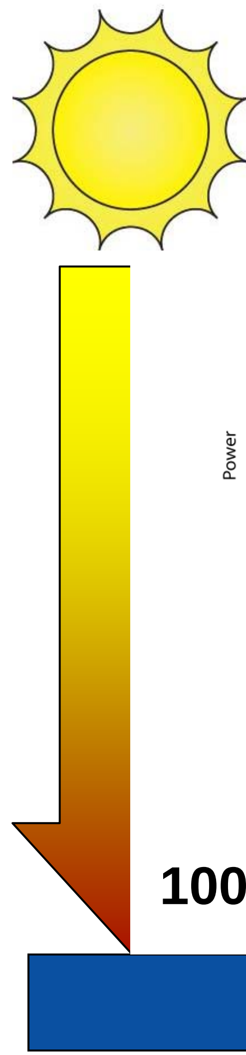
ΔT = 500º

η_{real} ~ 25%

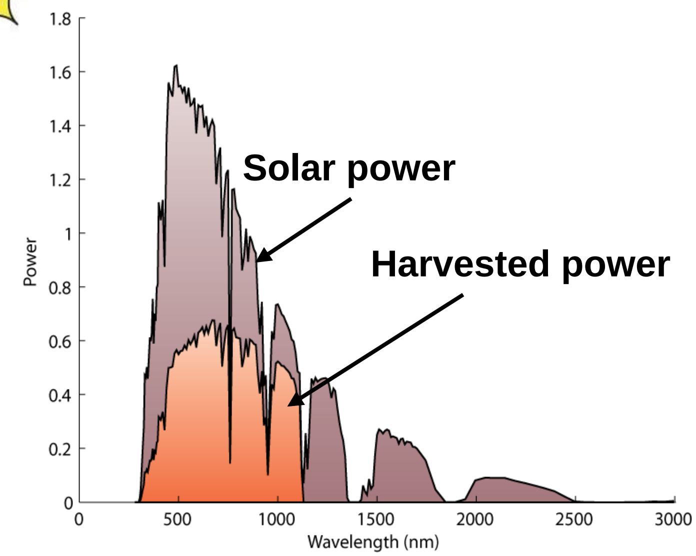
100º C

- **Full use of low grade heat**

Photovoltaics



5800º C



100º C

- absorption losses
- thermalization losses

η_{real} ~ 20%

- **Partial use of high grade heat (high per-quanta energy)**

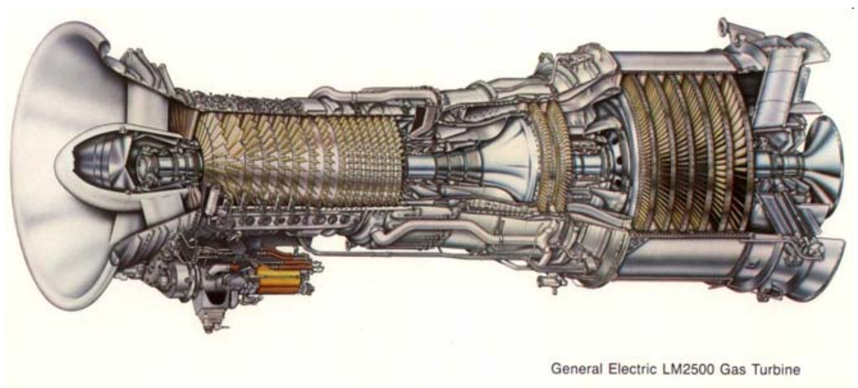
How *Efficient* are fossil fuels?

Coal Plants are ~33% efficient.

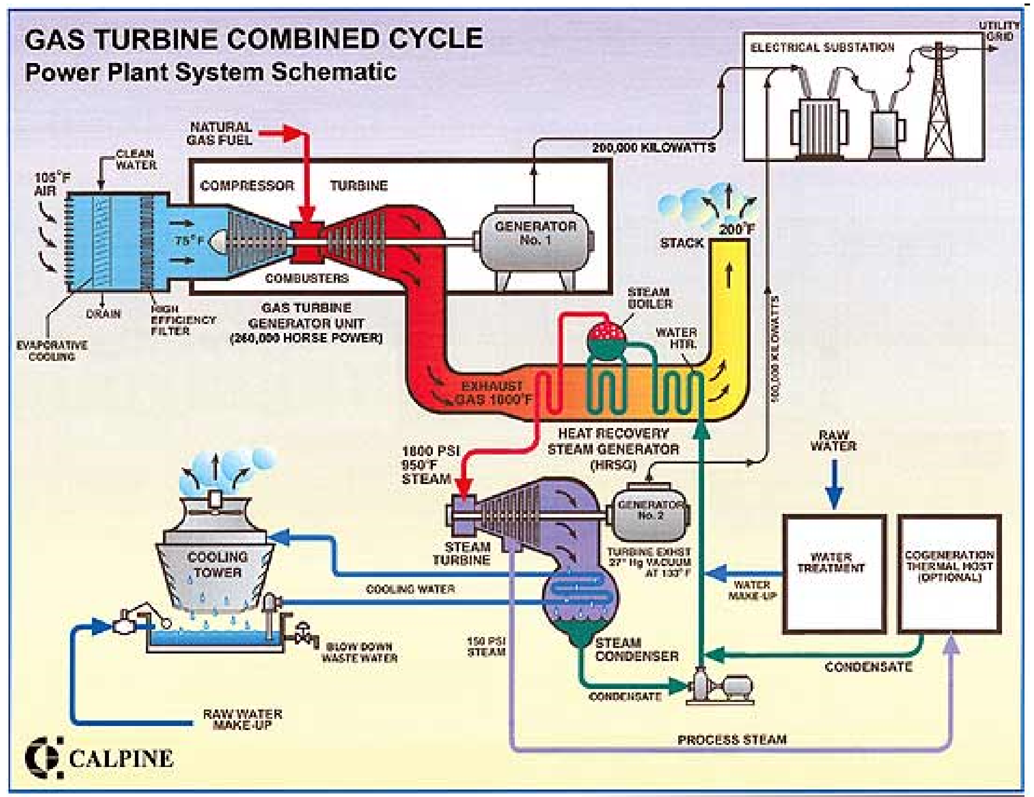
Natural Gas Plants are > 53% efficient!

How come?

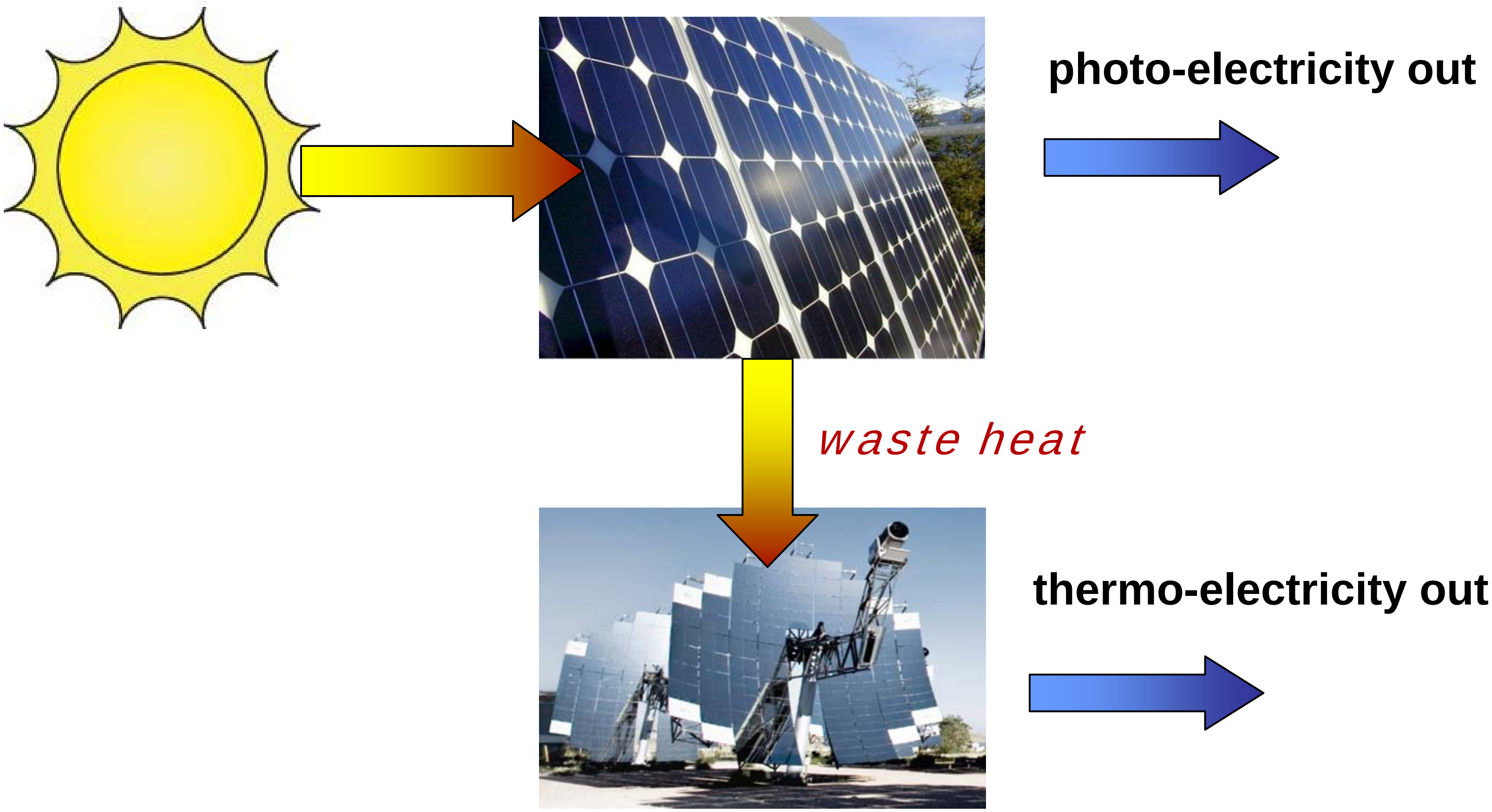
Combined Cycles!



A GE gas turbine

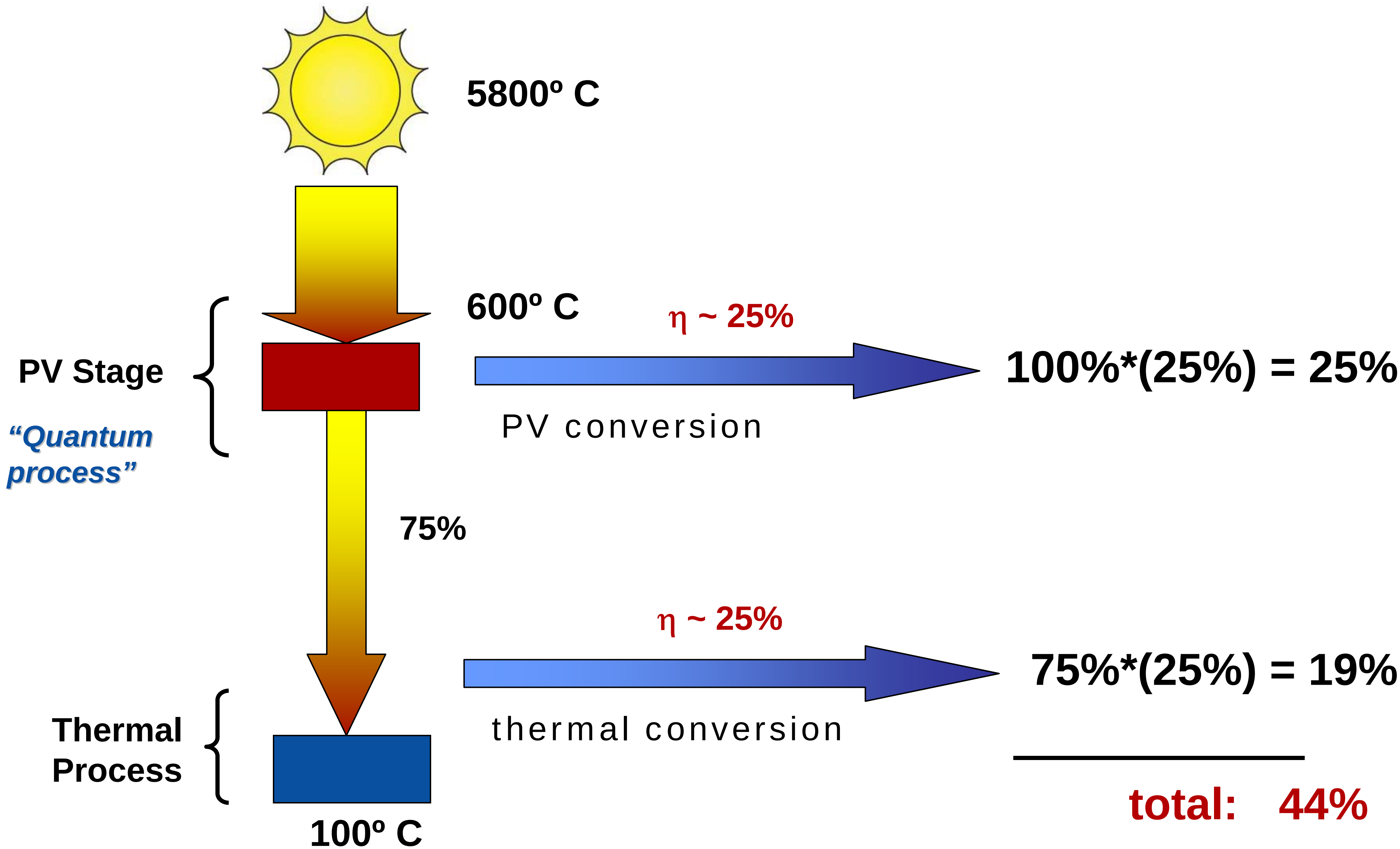


A Better Way: Combined Cycles



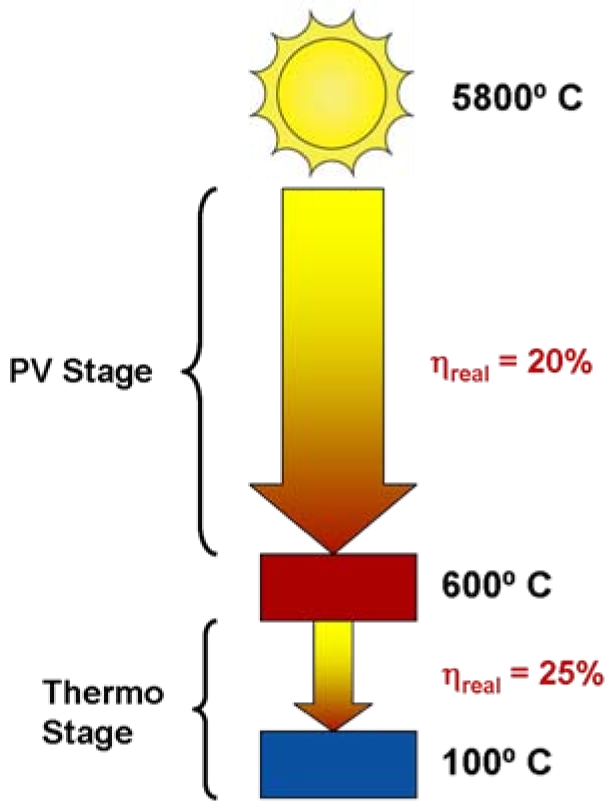
Premise: A high-temperature photovoltaic combined with a thermal engine is the most effective way to maximize output efficiency.

Combined HT-PV/ Thermo Cycle



Combined cycles can take two modest performance devices to form a very high efficiency device.

High-Temperature PV



The key is to develop a PV cell that can operate at high temperatures

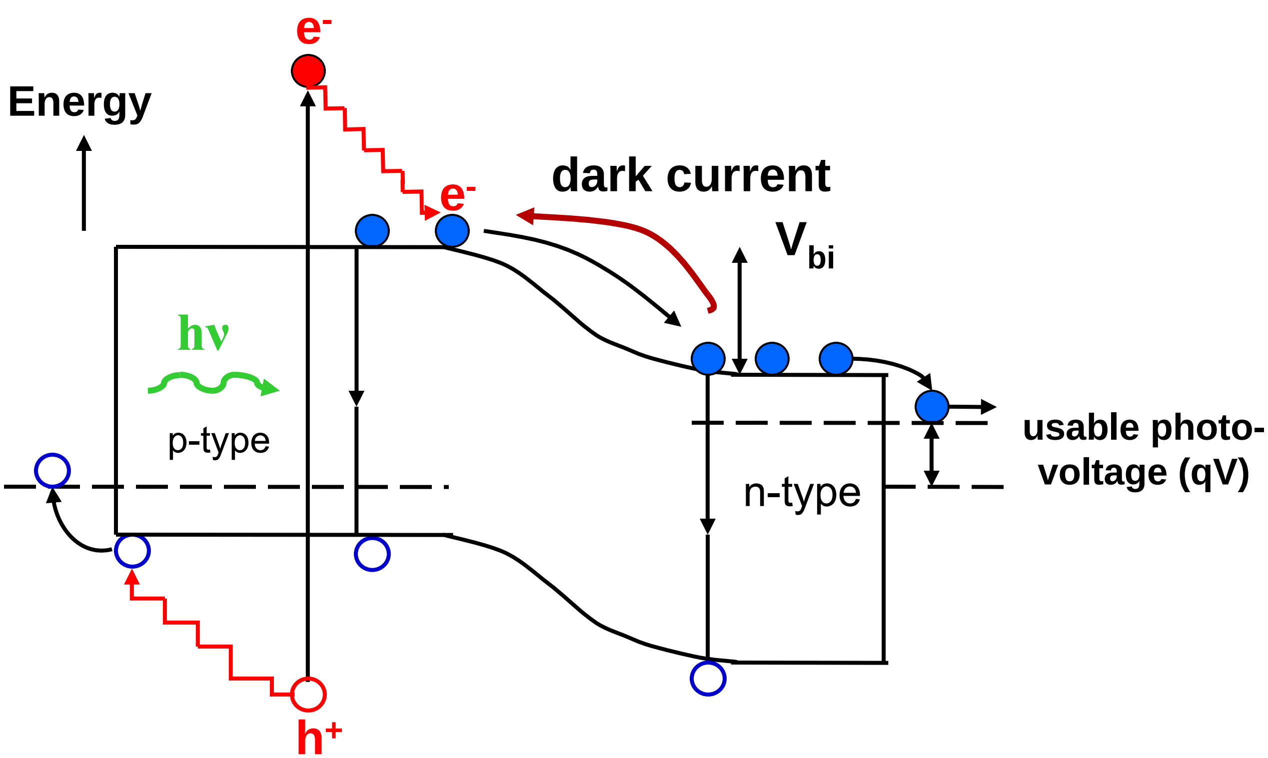
- **A 20% efficient High Temperature-PV (HT-PV) would increase current thermal performance by 60%**
- **Current ~12¢/kWh LCOE could decrease to ~7¢/kWh**
- **Possibly add on to existing designs**

Can we make a High-Temperature Photovoltaic?

No.

PV at High Temperature

PV does not operate well at high temperatures!



Ideal Diode equation:

$$J = J_{SC} - J_0\left(e^{eV/kT} - 1\right)$$

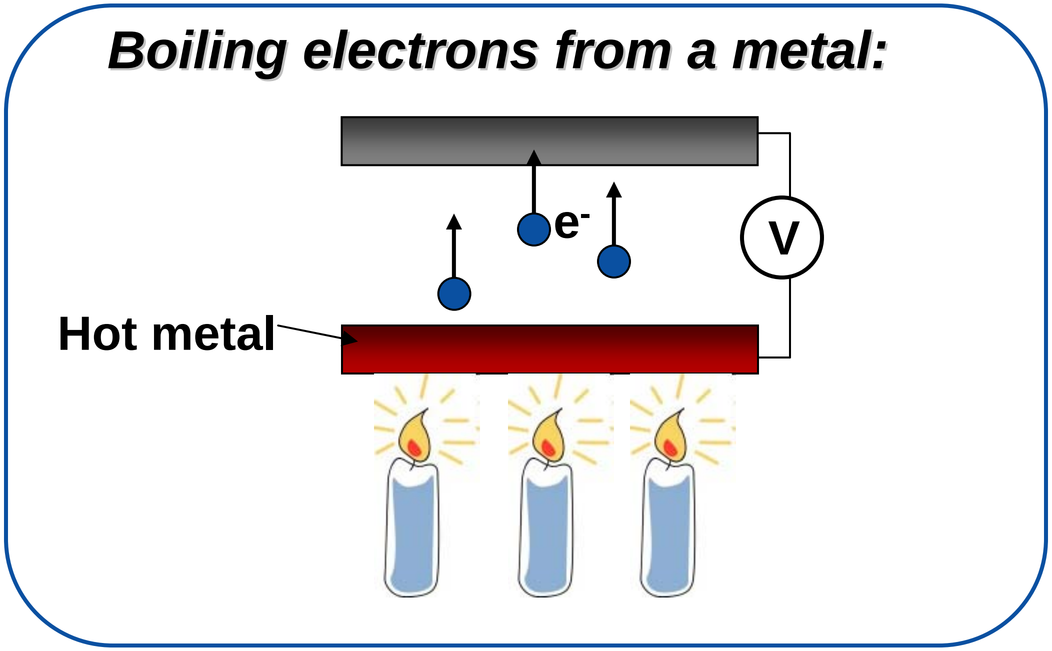
Carrier generation

Dark current

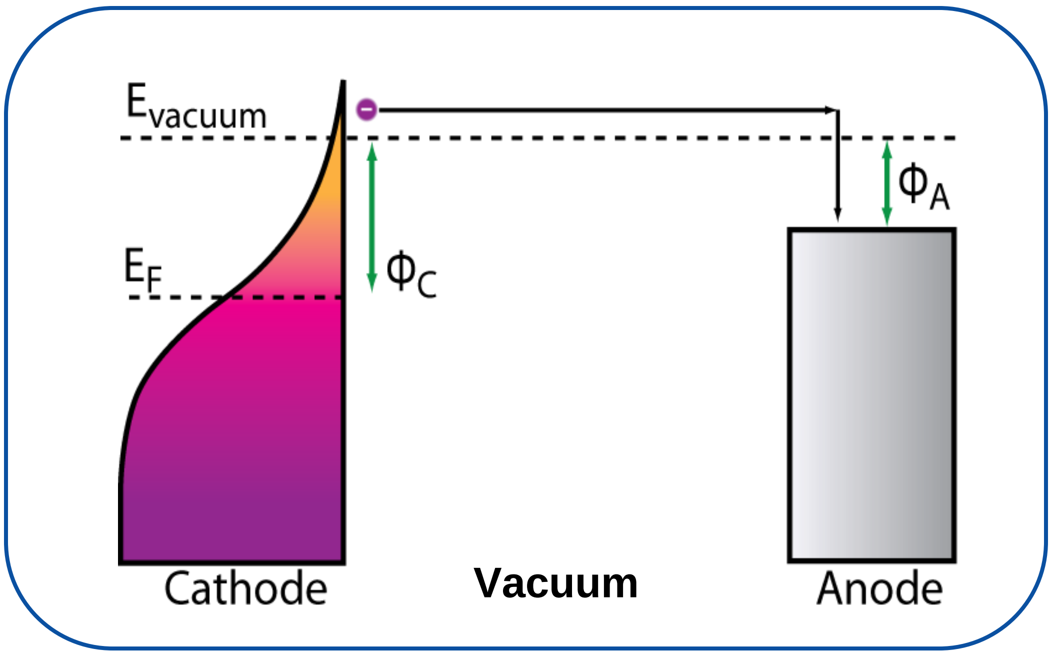
We need a device that can use large per quanta photon energy (like PV), and combine it with the high temperature operation and thermal harvesting.

What processes can operate at high temperatures?

Thermionic Emission



- Operates at very high temperatures; generally >1200ºC
- Robust; long service lifetimes
- Low output voltages



- $J = AT^2 \, e^{-\phi C/kT}$
- $P = J\,(\phi_C - \phi_A)$

Thermionic Emission: History




- Thomas Edison in 1880 describes "the flow of charged particles called thermions from a charged metal or a charged metal oxide surface, caused by thermal vibrational energy"
- Sir J.J. Thompson discovers electrons in his cathode-ray tubes experiments done in 1897, receives 1906 Nobel Prize
- Sir J.A. Fleming develops a thermionic vacuum tube and patents the first diode in 1904
- O. Richardson develops thermionic emission model (1902), winning the 1928 Nobel Prize "for his work on the thermionic phenomenon and especially for the law named after him."

$$J = AT^2 e^{-\Phi_E / kT}$$ (Richardson-Dushman law)

J = current density (Acm^{-2}), Φ_E = emitter work function (eV)

Thermionic Devices

TOPAZ Satellite (circa 1980's)

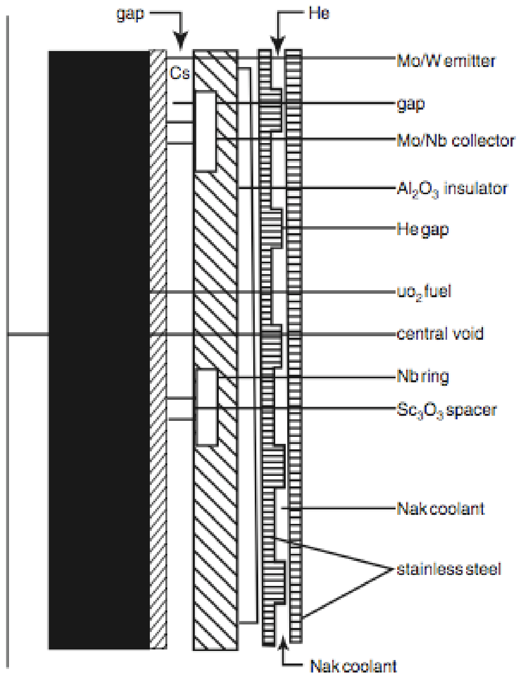
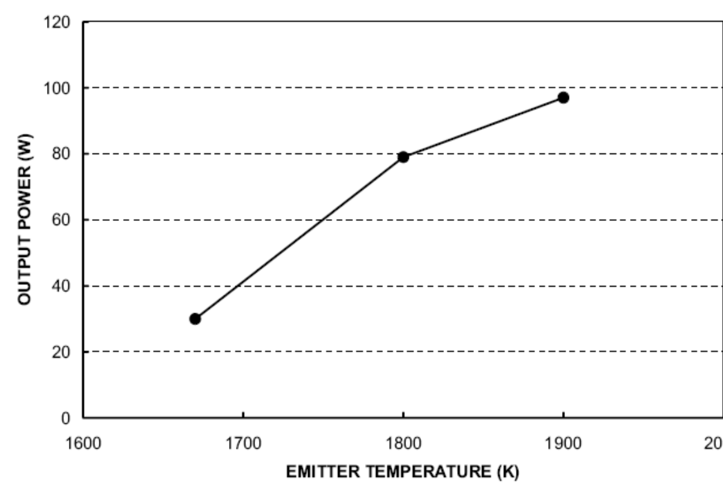


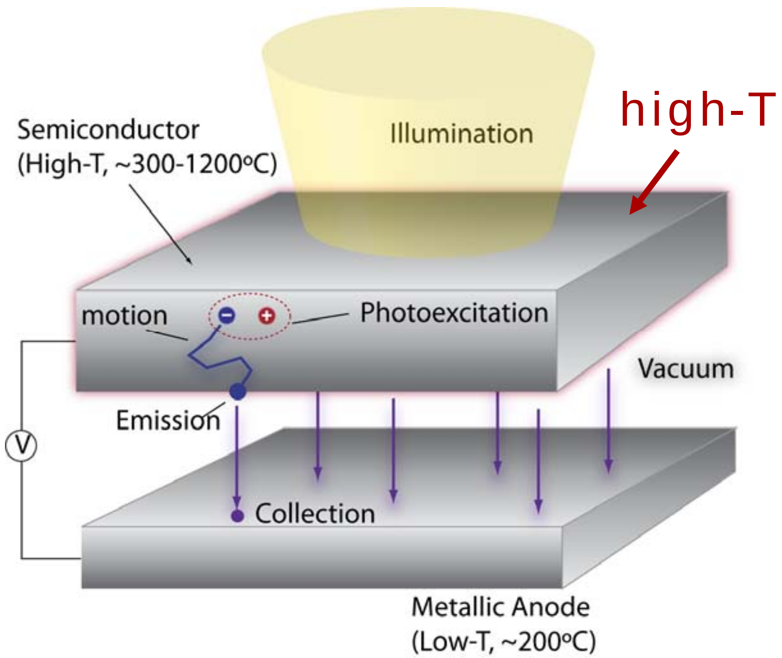
Fig. 1 *The cross-section of the TOPAZ-II TFE*

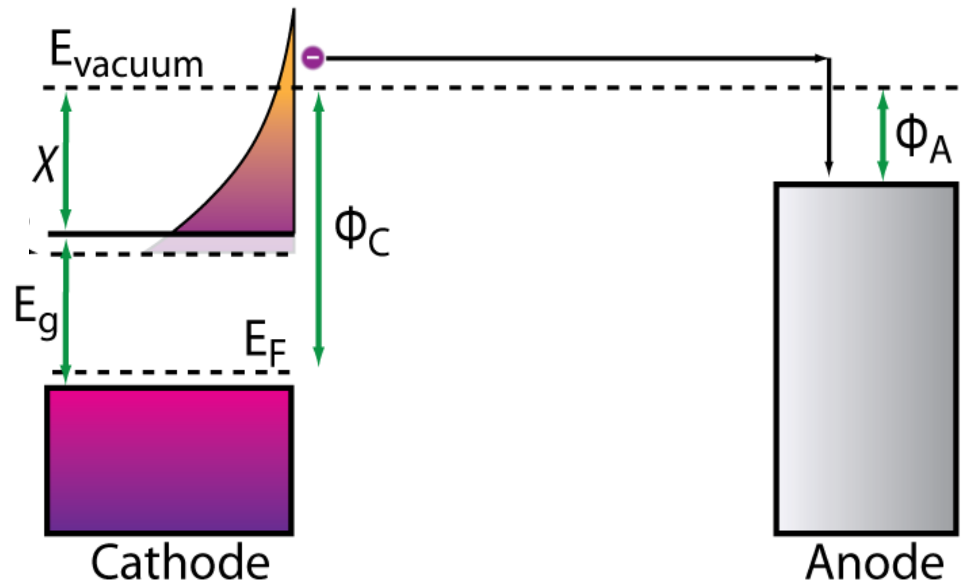
- Work in the US and USSR space programs culminated in the Soviet flights of 6 KW TOPAZ thermionic converters in 1987
- Source of heat: nuclear pile
- Basic technology: vacuum tubes
- Machined metal with cathode-anode distance (>100 μm) and required cesium plasma

Solar Testing (circa 2000)



Photon Enhanced Thermionic Emission (PETE)

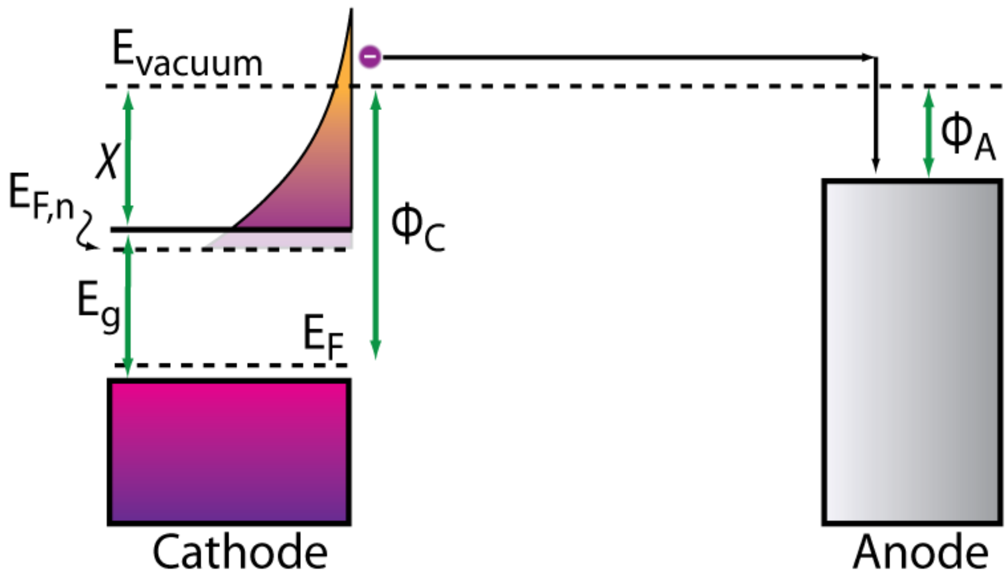




- **Photo-excite carriers into conduction band**
- **Thermionically emit these excited carriers**
- **Overcome electron affinity barrier (not full work-function)**
- **Collected at low work-function anode**

Schwede et al, Nature Materials, 9 ,762–767, 2010

Photon Enhanced Thermionic Emission (PETE)



Thermionic Current:

$$J = AT^2 \exp\left(\frac{-\phi_c}{kT}\right)$$

PETE Current:

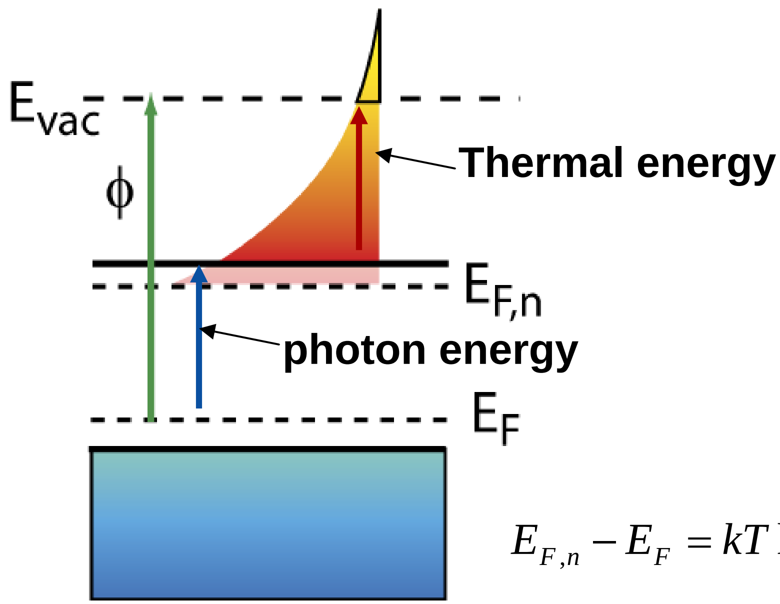
$$J = AT^2 \exp\left(\frac{-\phi_c}{kT}\right) \exp\left(\frac{\Delta E_F}{kT}\right)$$

$$J = AT^2 \left(\frac{n}{n_i}\right) \exp\left(\frac{-\phi_c}{kT}\right)$$

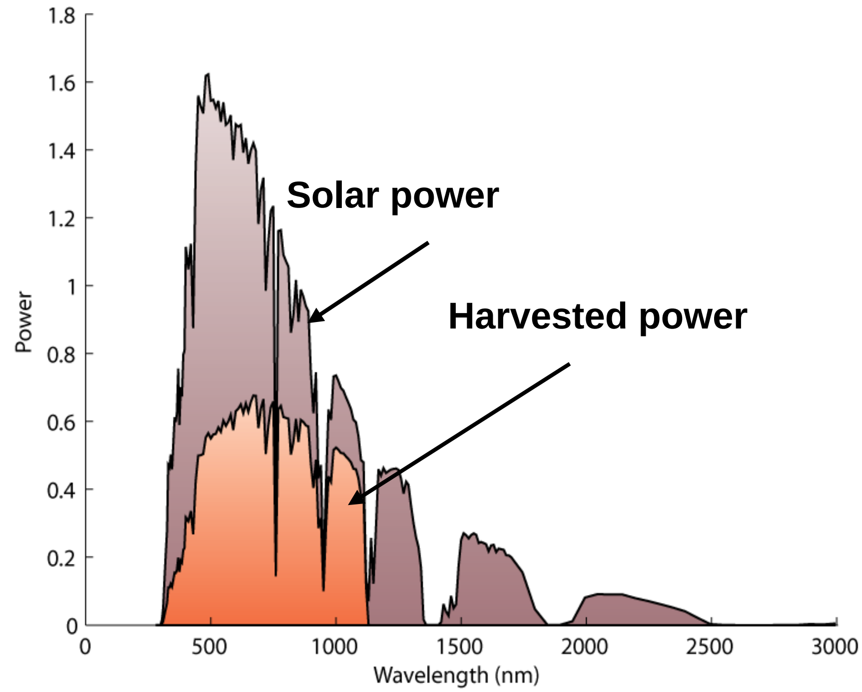
If E_g = 1.4 eV, then at 300º C:

- $J_{pete}/J_{therm} = e^{\Delta E_f/kT} = 1.4\mathrm{x}10^9$

PETE vs PV



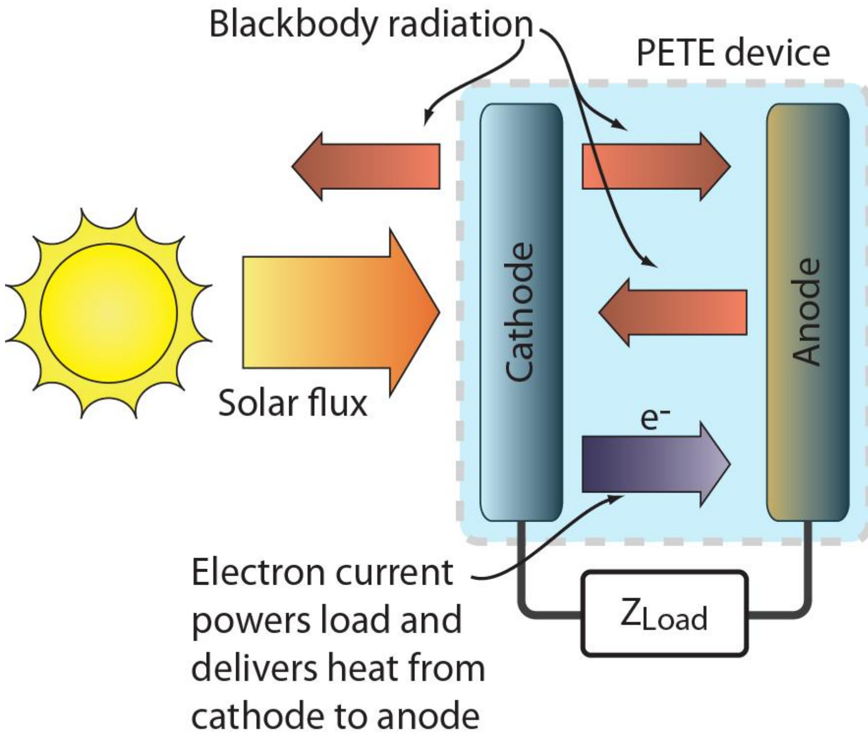
$$E_{F,n} - E_F = kT \ln\left(\frac{n}{n_i}\right)$$

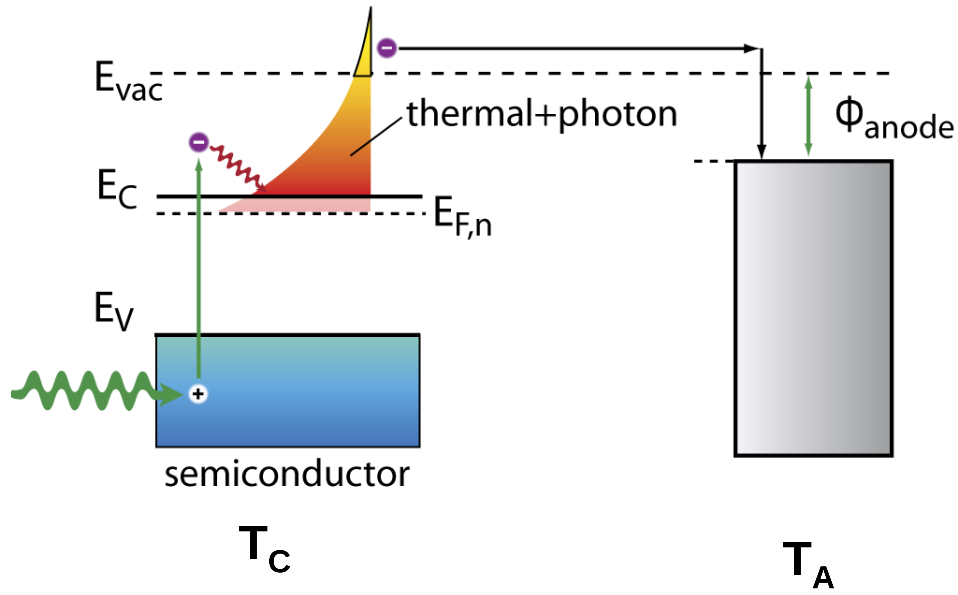


- **PETE harvests thermal and photon energy**
  - **sub-band gap, thermalization, and recombination “losses” collected**
- **Can operate at higher voltages**
- **Balance photon absorption and heat generation**
- **High temperatures beneficial- doesn’t degrade performance**

Seems good… but how do the actual numbers compare?

Full PETE Simulation

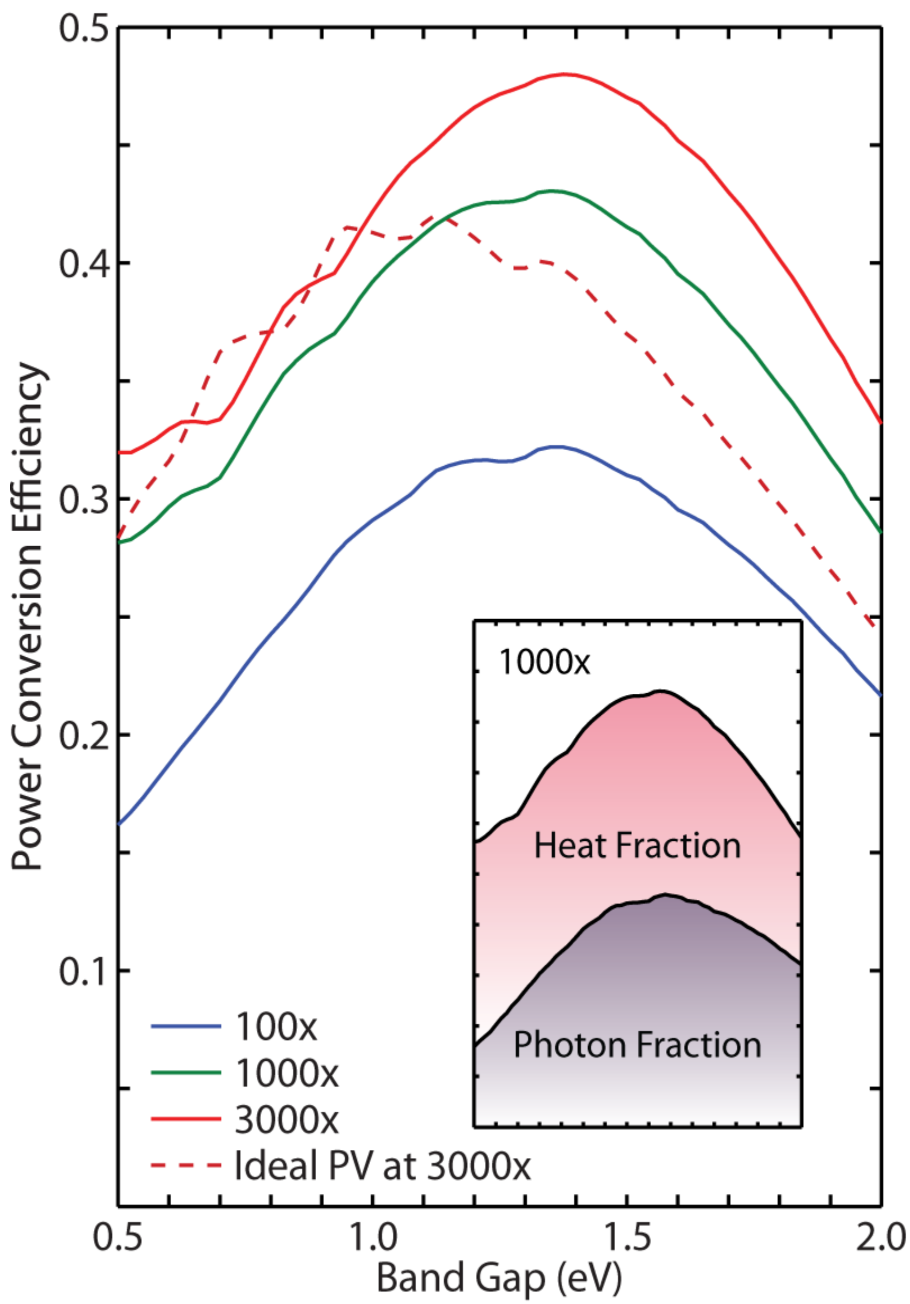


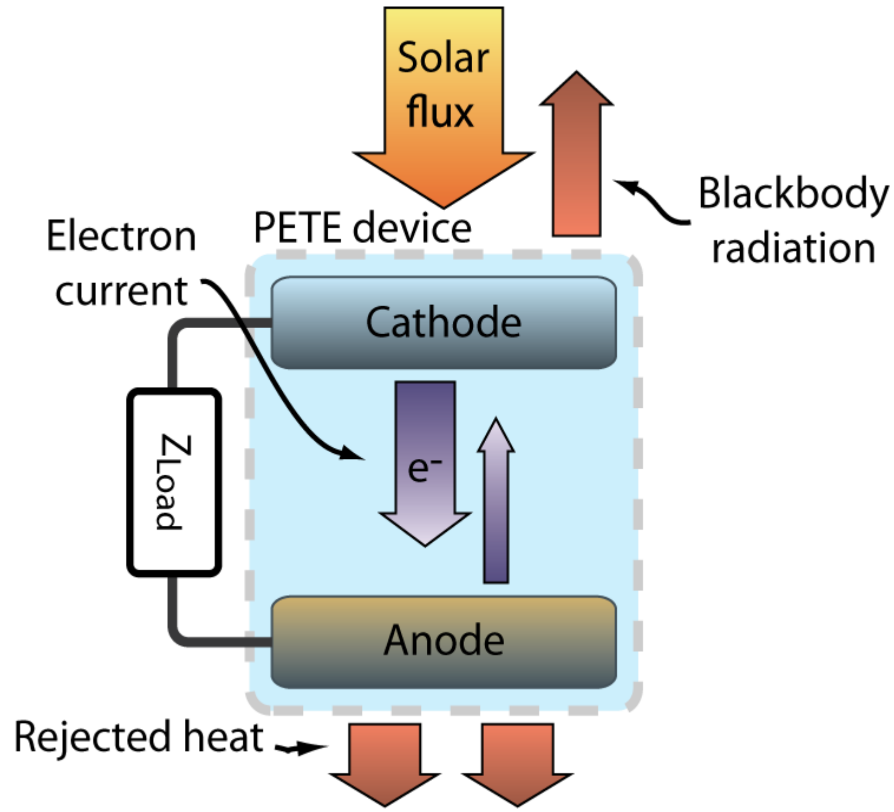


PETE calculations:

- **Each photon $h\nu > E_g$ is absorbed and excites one electron**
- **Sub-bandgap photons are absorbed as heat**
- **BB radiation losses and transfer included**
- **Radiative and Auger recombination losses (Si params) included**
- **'dark current' from anode treated as thermionic emission**
- **Variables: solar concentration, T_C, T_A, χ, E_g, ϕ_A,**

Theoretical Efficiency

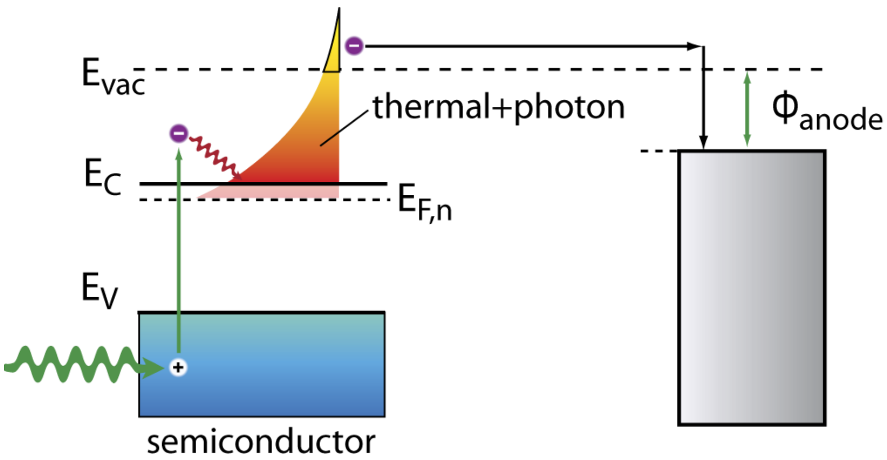


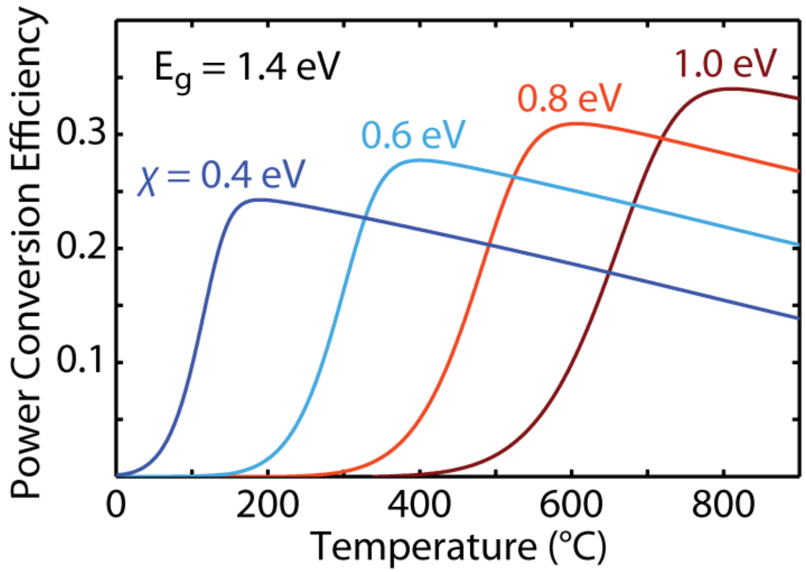


- To adjust: E_g, χ, T_C
- φ_A = 0.9 eV
  - [Koeck, Nemanich, Lazea, & Haenen 2009]
- $T_A \leq 300°C$
- Other parameters similar to Si
  - 1e19 Boron doped

Schwede et al, Nature Materials, 9 ,762–767, 2010

Maximizing PETE performance





$$E_{F,n} - E_F = kT \ln\left(\frac{n}{n_i}\right)$$

Maximize $E_{F,n}$:

- **High solar concentration**
- **Low recombination rates; electrons emit before relaxing**

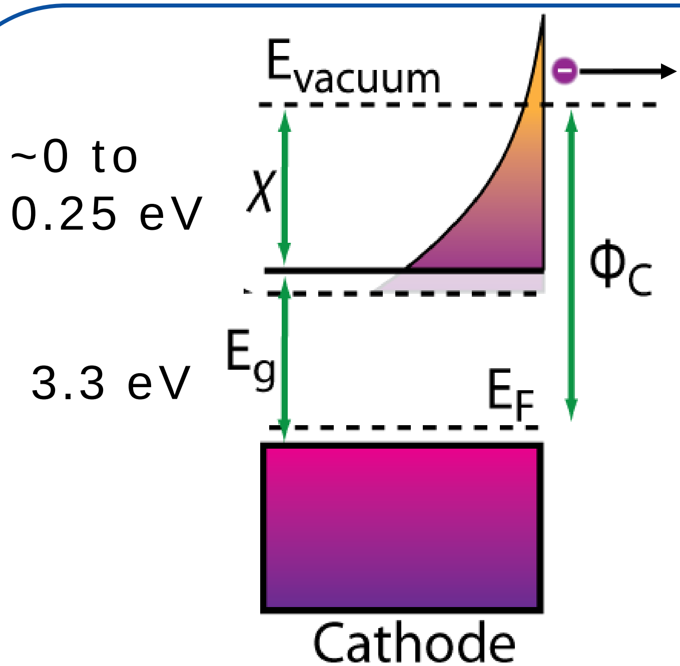
Maximize V:

- **Highest χ possible while still getting good electron yield at given T**
- **Minimize anode work function**

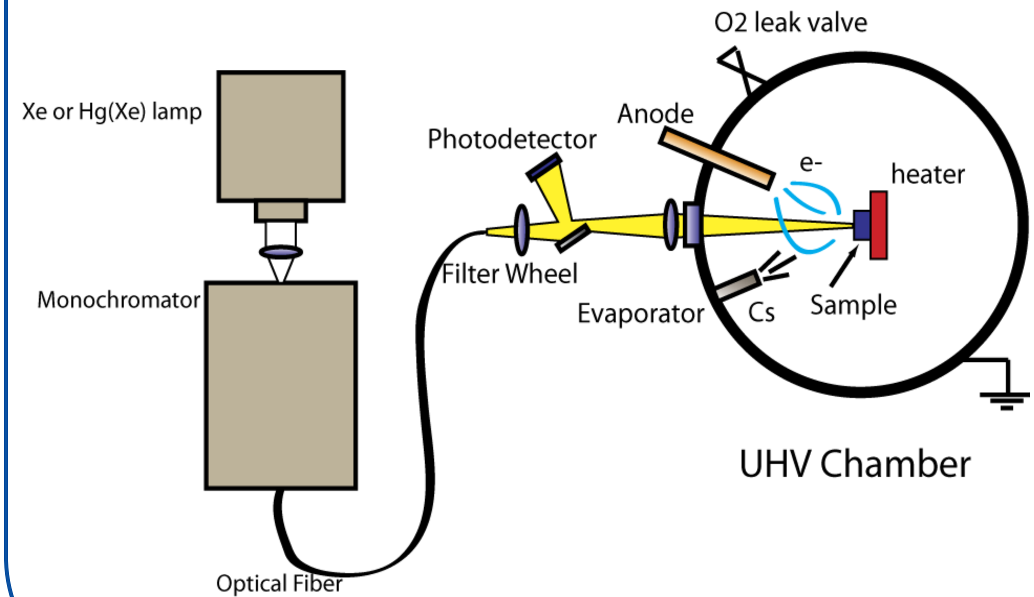
Maximize performance by controlling χ with surface coatings

Experimental Demonstration

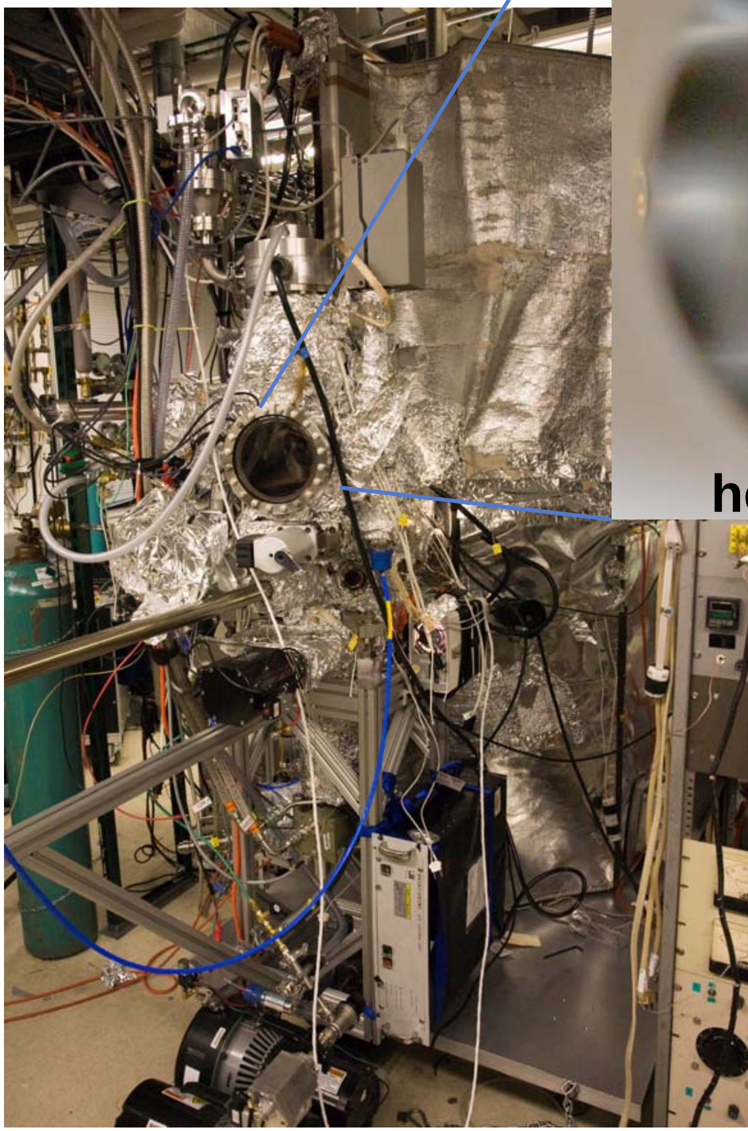
- [Cs]GaN thermally stable
  - Resistant to poisoning
  - E_g = 3.3 eV
  - 0.1 μm Mg doped
  - $5x10^{18}$ cm^{-3}

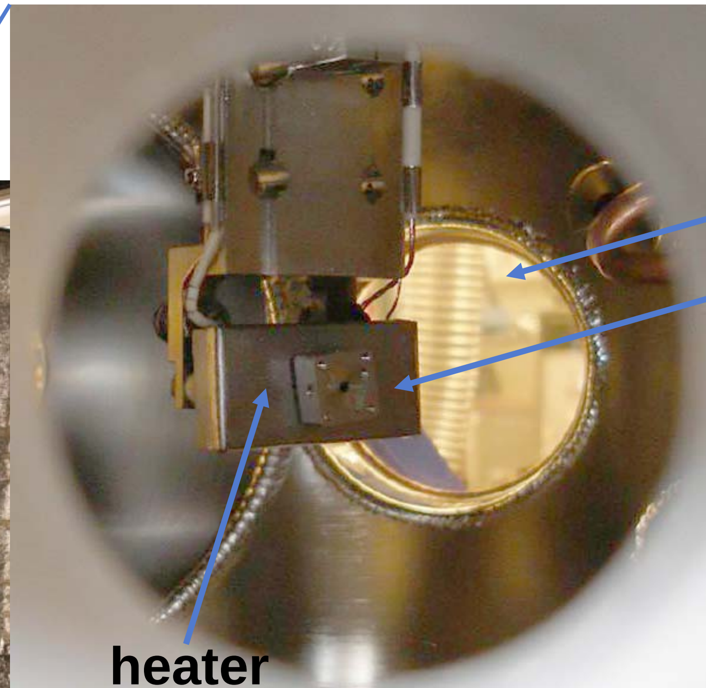


Experimental Apparatus:



Experimental Apparatus





heater

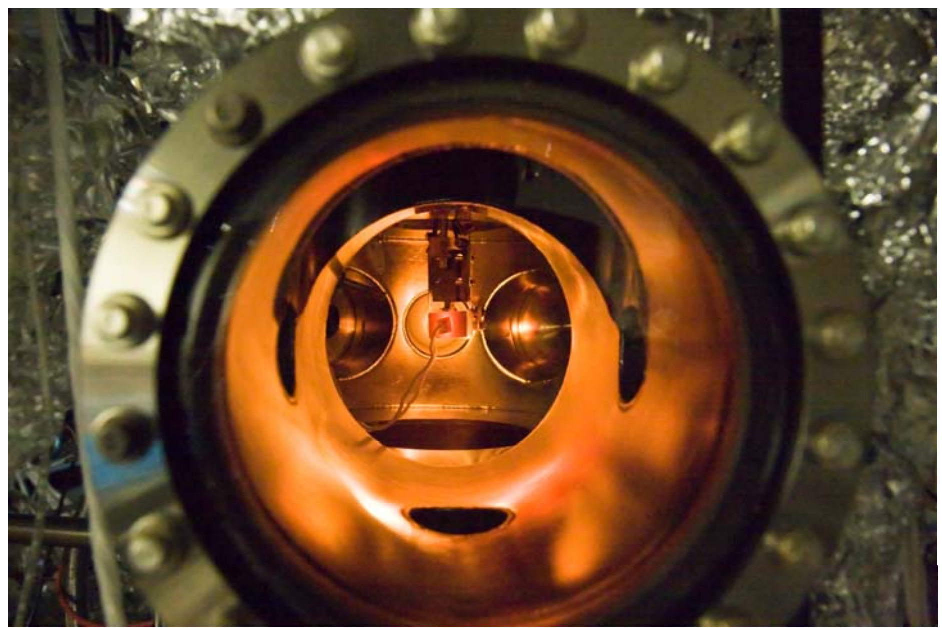
optical access

removable sample mount

not visible:

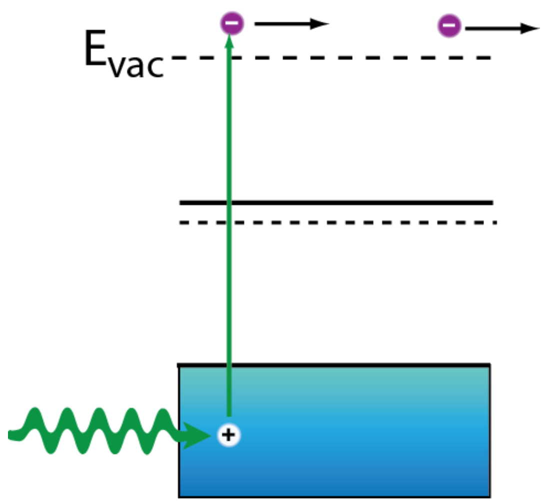
- anode

- Cs deposition source

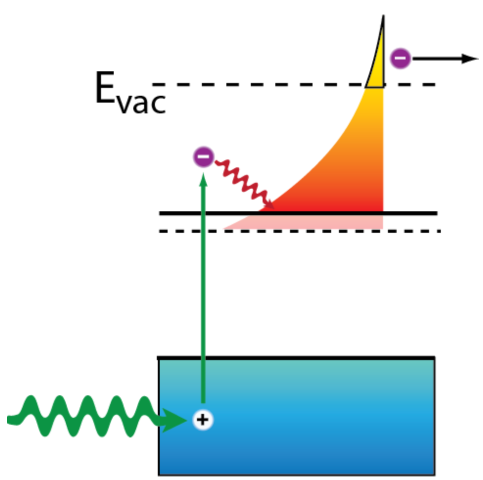


PETE or Photoemission?

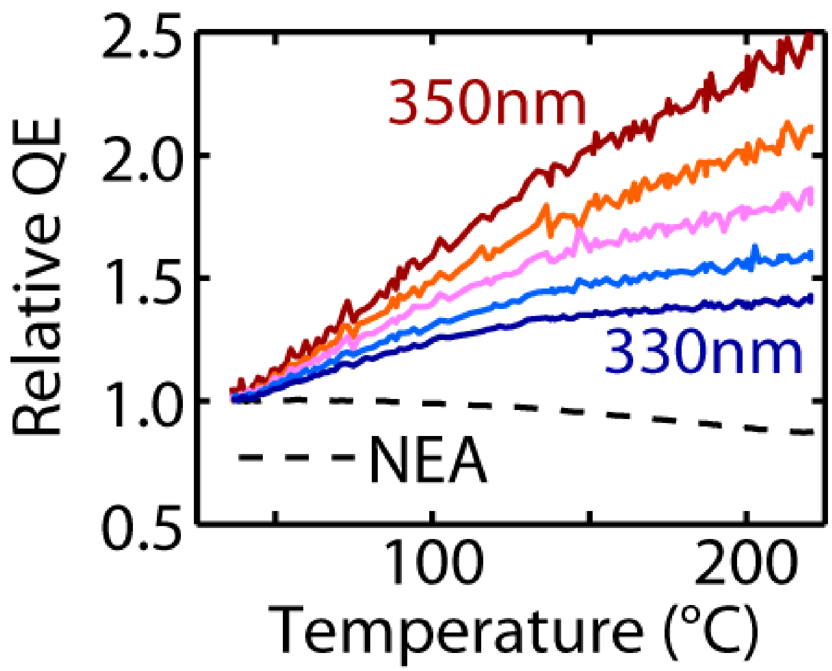
Direct Photoemission



PETE:



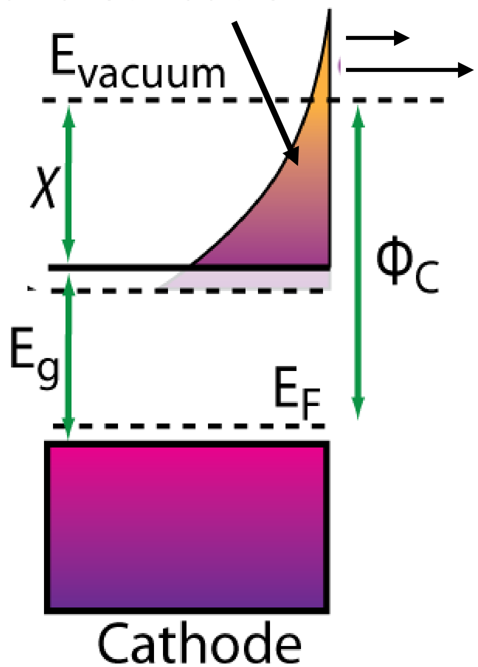
Temperature Dependent Yield

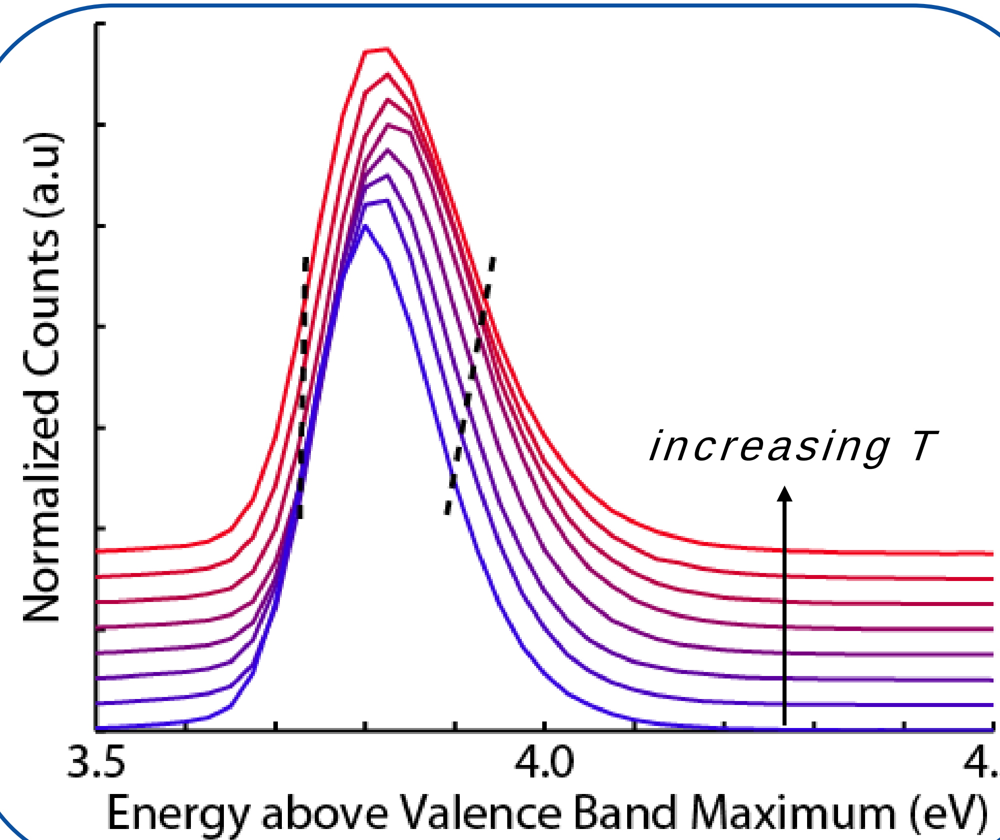


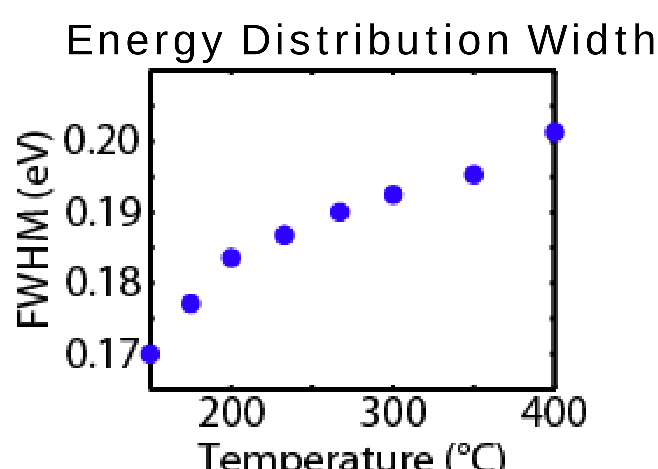
- PETE or photoemission?
- Direct Photoemission:
  - Yield decreases with increasing T
  - Electron energy independent of T
  - Electron energy depends on wavelengths

T-Dependent Emission Energy

- PETE electrons should show thermal distribution
- Distribution should broaden with temperature
- Measure emitted electron energy







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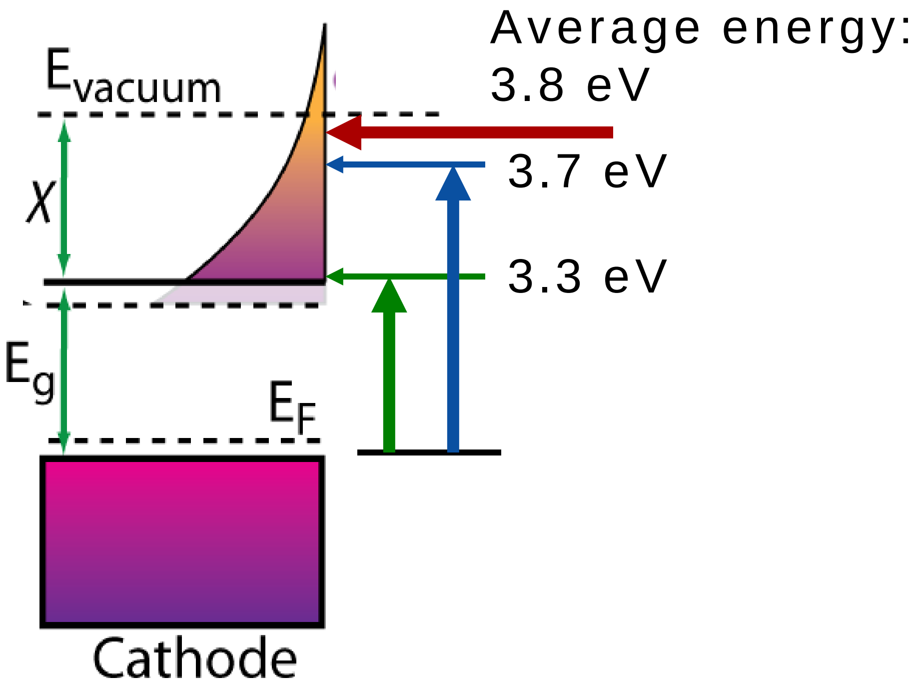
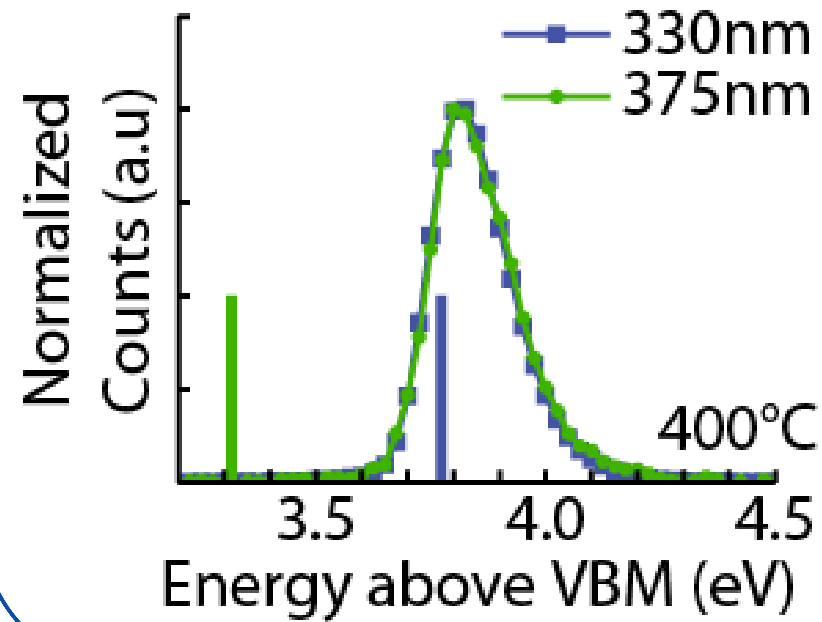
Photon-independent Emission Energy

- Photon energy should not matter above band gap
- Very different from photoemission
- Green = just above gap
- Blue = well above gap, not above E_{vac}



Energy distribution for different excitation energy



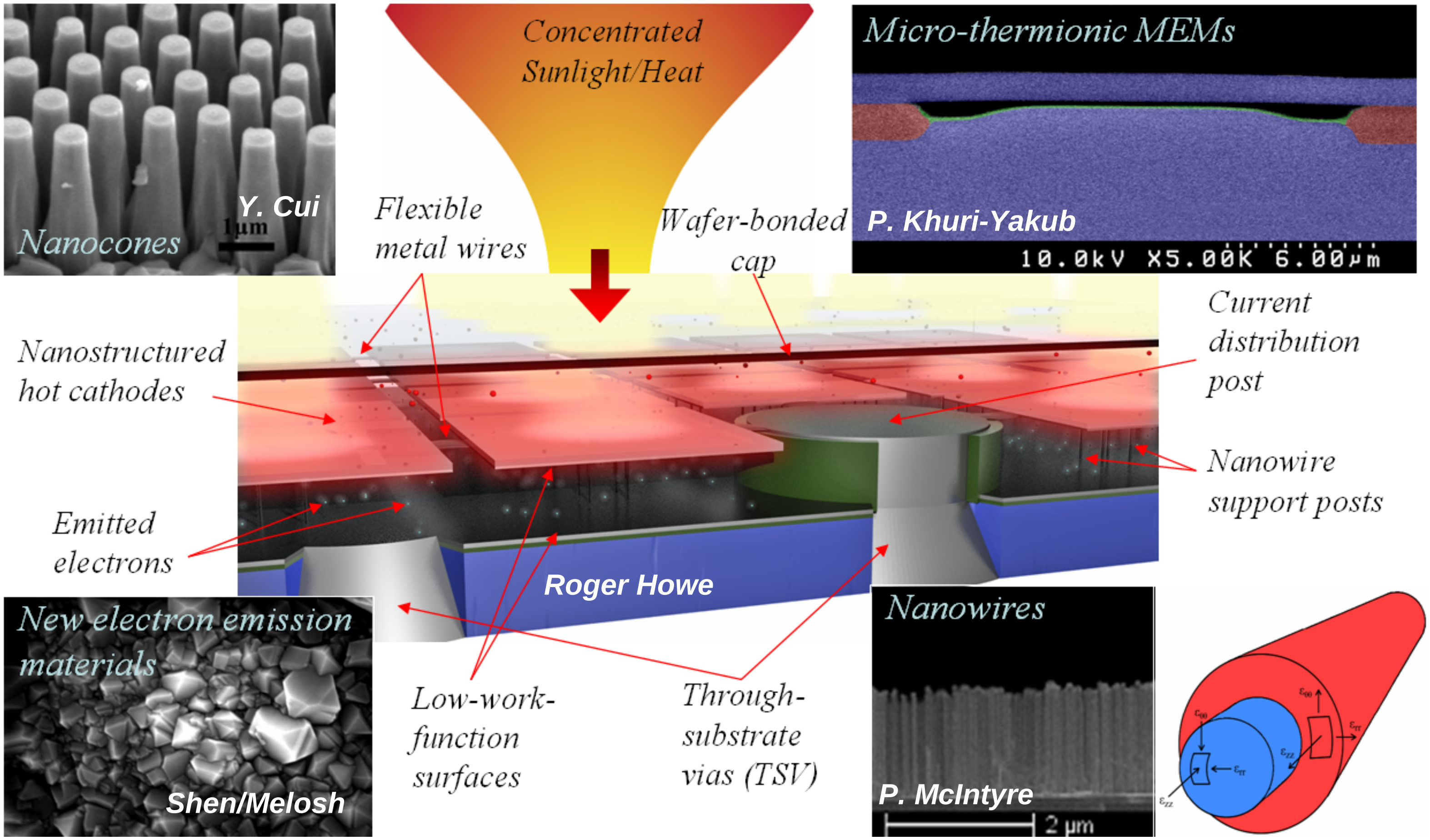
- Identical energy distributions
- 0.5 eV thermal voltage boost significant
- 400ºC = 0.056 eV

Evidence for PETE

- Yield dependence on temperature
  - decreases for direct photoemission
  - *increases for above gap, but sub-ionization energies*
- Emitted electron energy increases with temperature
  - >0.1-0.2 eV higher than photon energy
- Electron energy follows thermal distribution
- 330nm and 375nm illumination produce same electron energy distributions at elevated temperature
  - electrons harvested up to 0.5 eV additional energy from thermal reservoir

What would PETE look like?

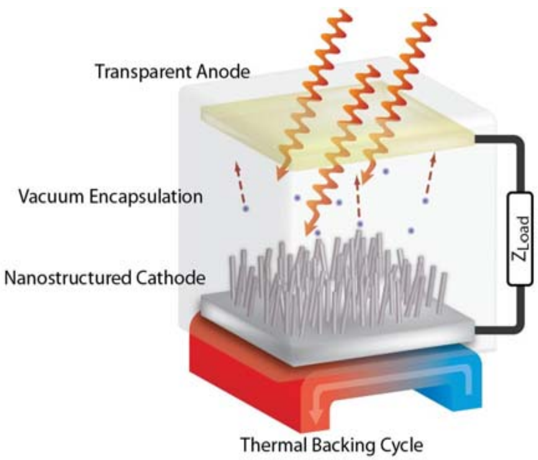
Most efficient: Combine MEMs and nanotechnology

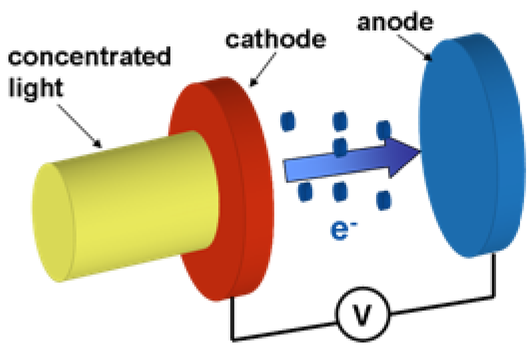


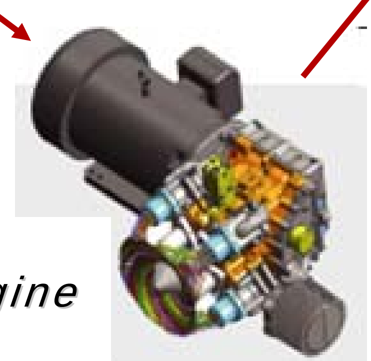
with Prof. Roger Howe, Dr. Igor Bargatin

Adding PETE onto Existing Equipment

PETE device





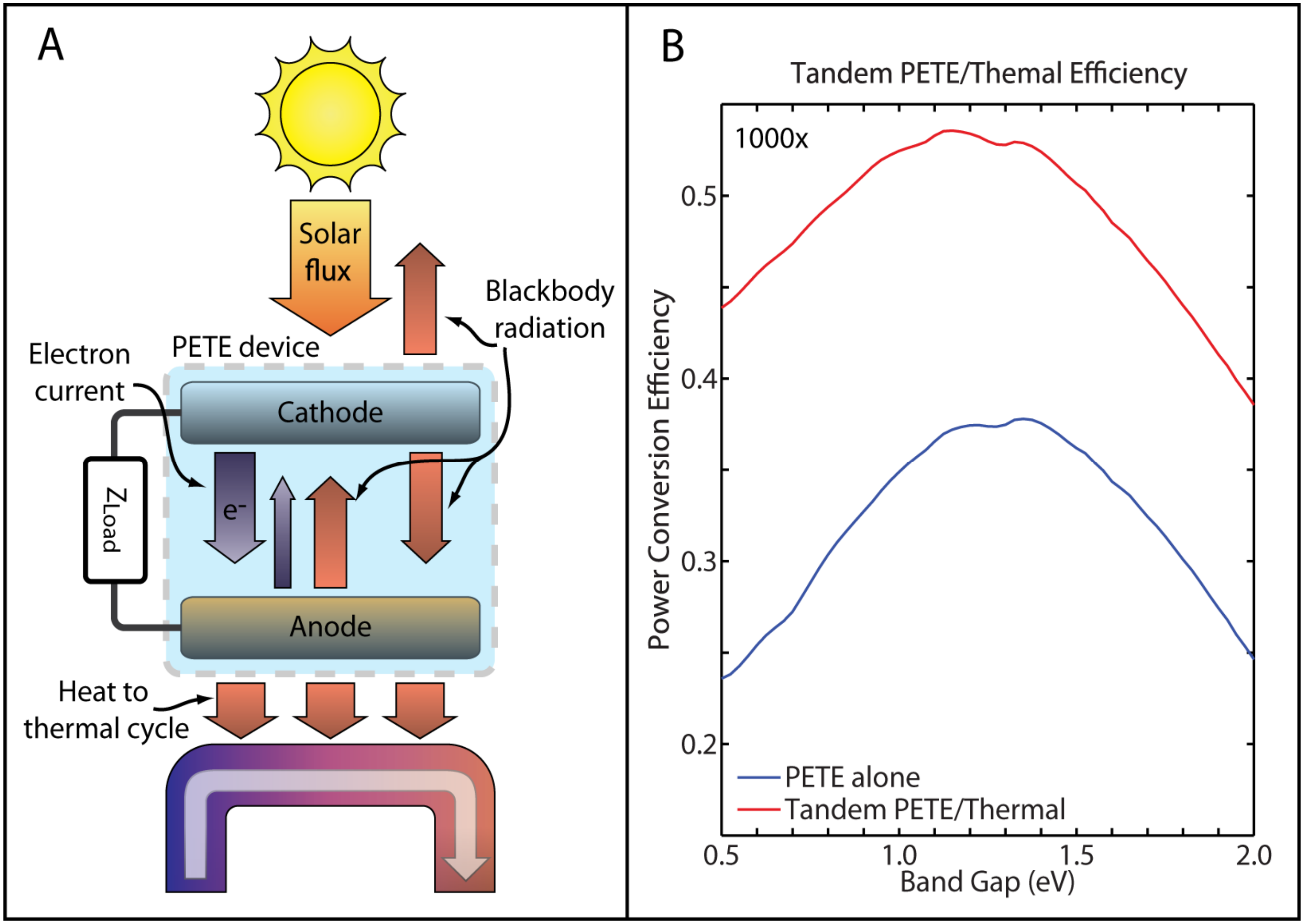


Stirling engine

Tessera 20 kW Stirling concentrator dish

- Several companies already operate Stirling-based CSP
- Record: 32% efficiency; annual efficiency ~23% to grid
- Add PETE front stage, thermally connect anode, cathode or both
- Use nanostructured PETE cathode to absorb light and emit electrons

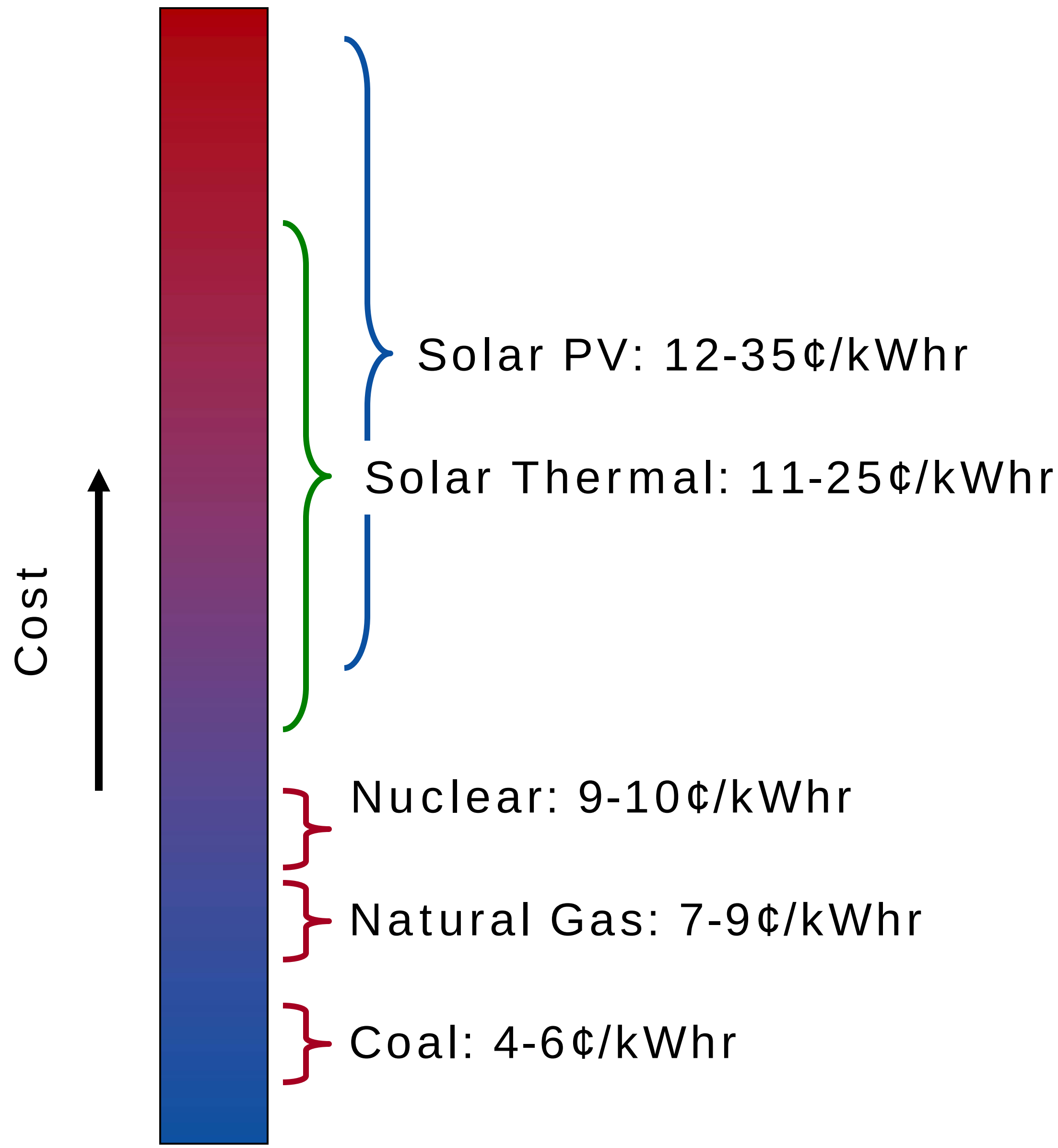
Theoretical Tandem Efficiency



31.5% Thermal to electricity conversion [Mills, Morrison & Le Lieve 2004]

285°C Anode temperature [Mills, Le Lievre, & Morrison 2004]

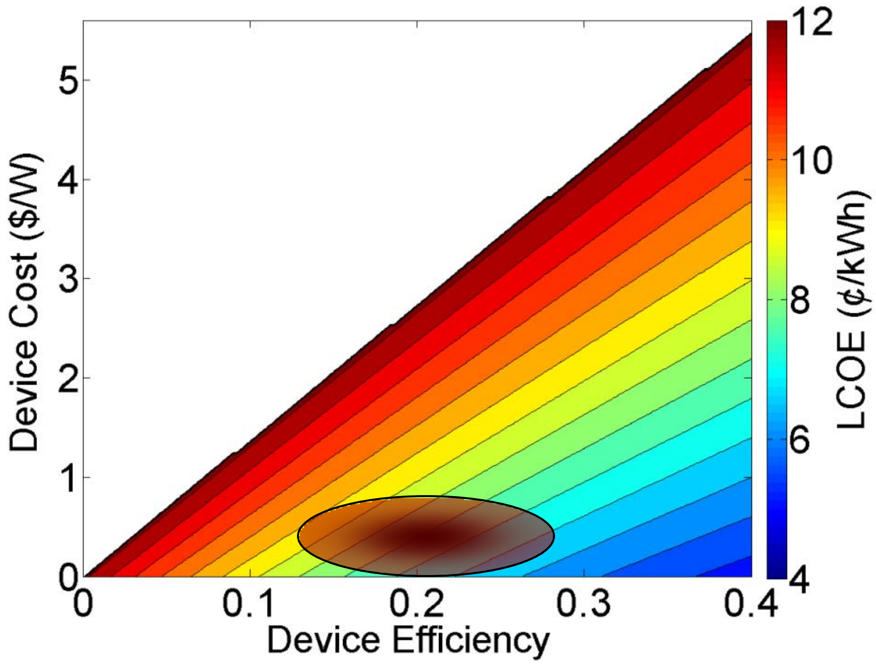
What efficiency do we *need?*

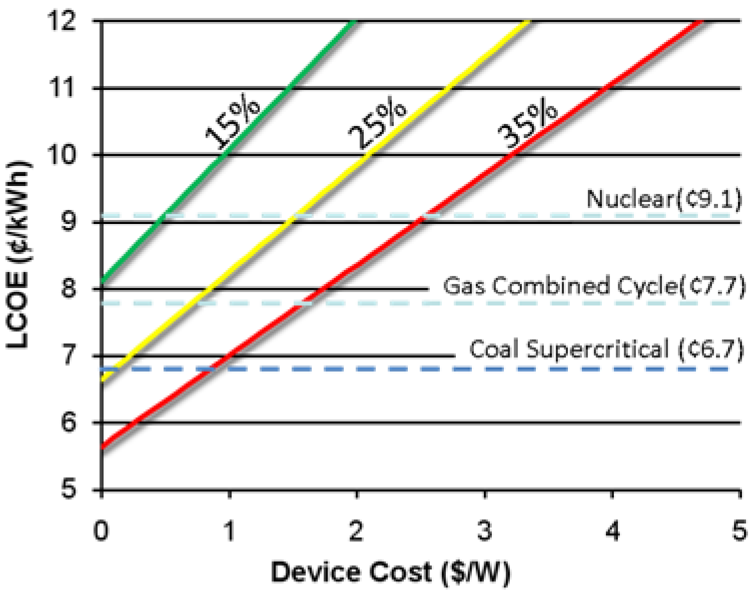


- High variability in estimates of renewable energy
- Want ~30-40% decrease in renewables cost

data: GCEP, IEA: “World Energy Outlook 2004”, California Energy Commission Report, 2007

Adding a PETE device





Based on NREL LCOE cost analysis of SunCatcher parabolic Dish array with additional PETE cost and efficiencies.

https://www.nrel.gov/analysis/sam/
http://www.energy.ca.gov/sitingcases/solartwo/documents/applicant/afc/volume_02+03/MASTER_Appendix%20B.pdf

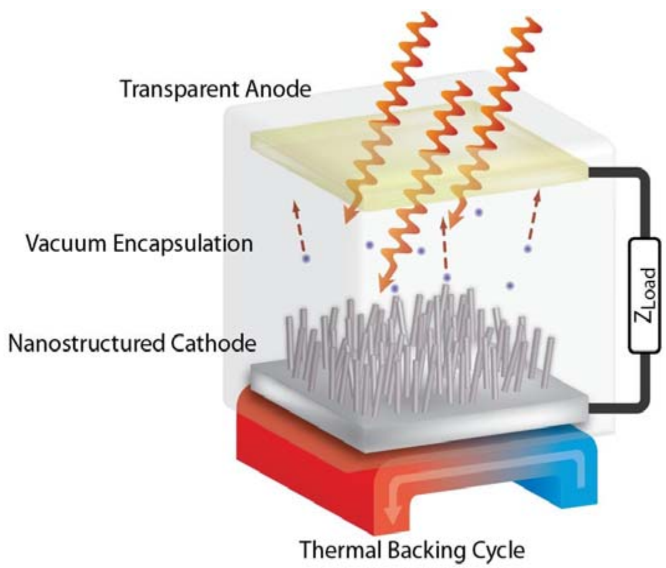
Cost Estimates:

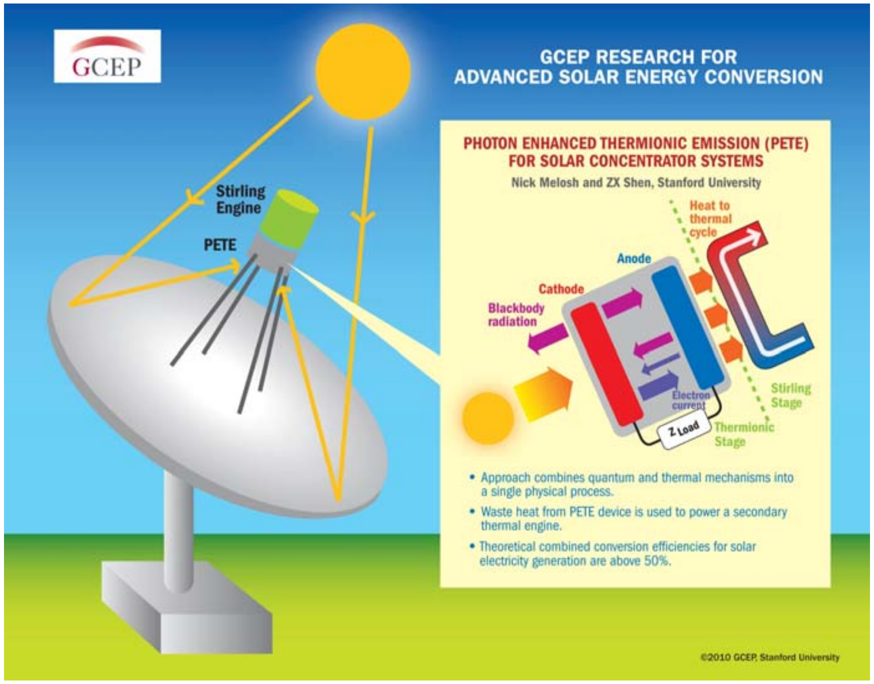
- **Original SunCatcher LCOE = 12¢/kWh**
- **An 20% PETE module estimated cost $25,000 for a 50kW plant**
- **~$0.50/kW additional cost to dish**
- **160% efficiency compared to thermal**
- **LCOE = ¢7/kWh**

To compete with Natural Gas, PETE must be 15-20% efficient at ~$.50/W

Take Home Messages

- *Combined Cycles* may be practical means to greatly increase efficiency
- PETE is a new way to combine thermal and photon energy
- Modest PETE efficiency could make economic impact
- Nanostructuring could be an important way to increase efficiency





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