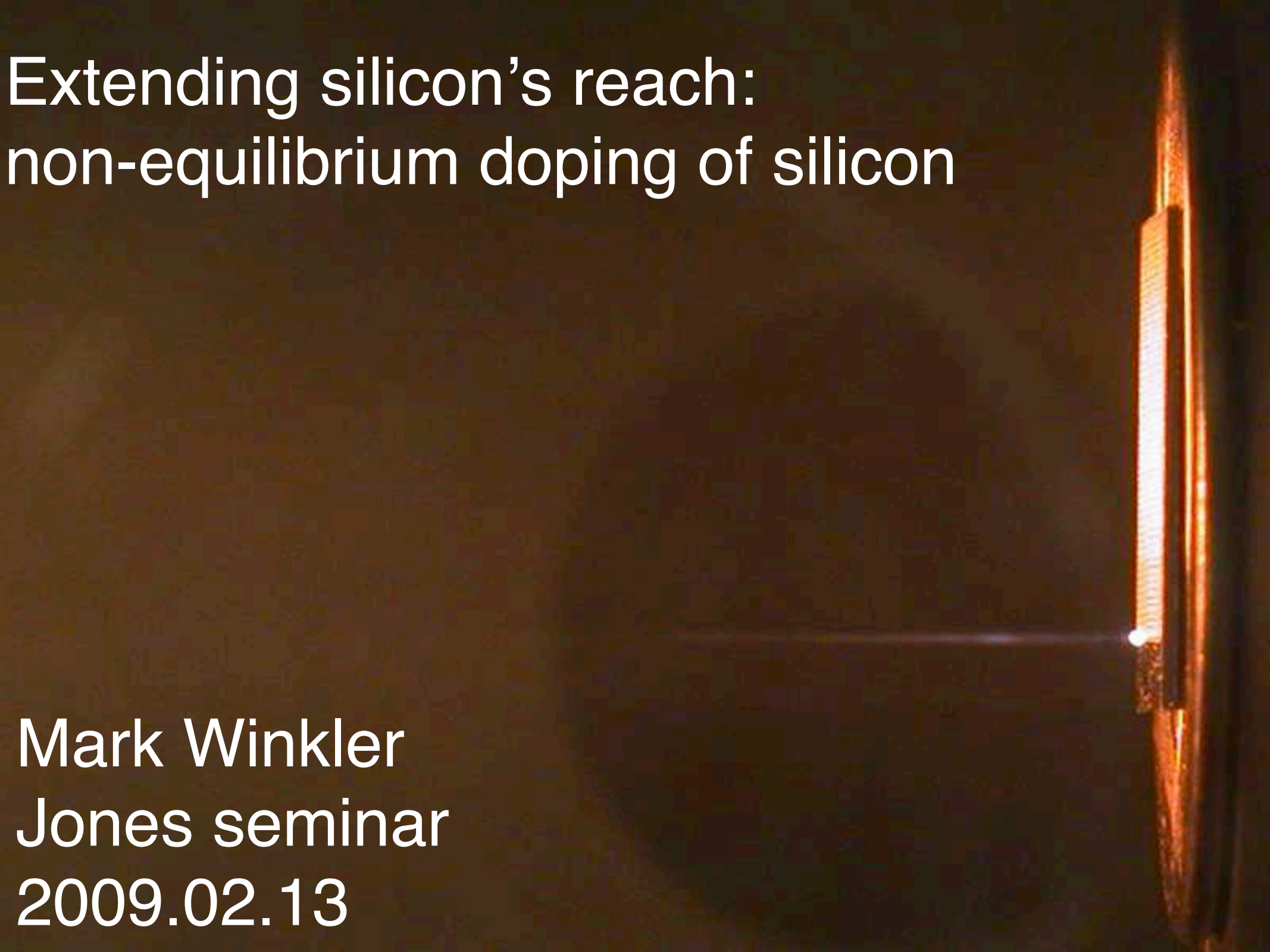
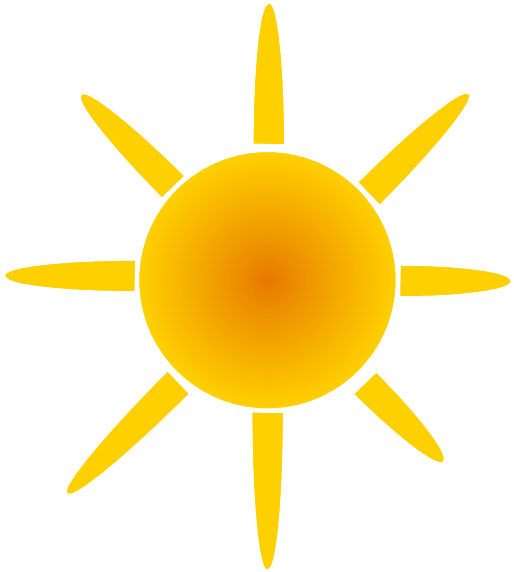
Extending silicon's reach: non-equilibrium doping of silicon



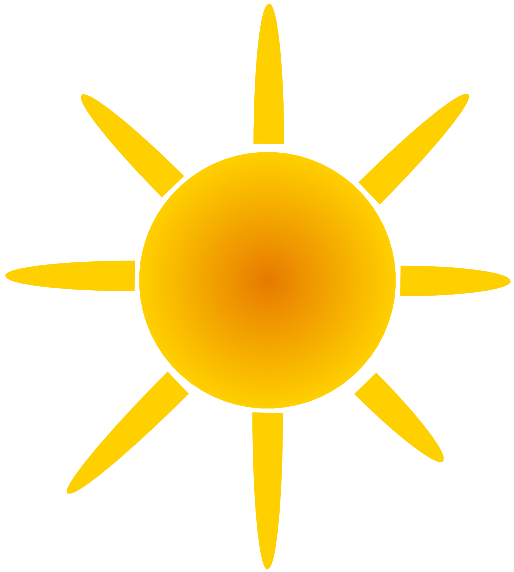
Mark Winkler

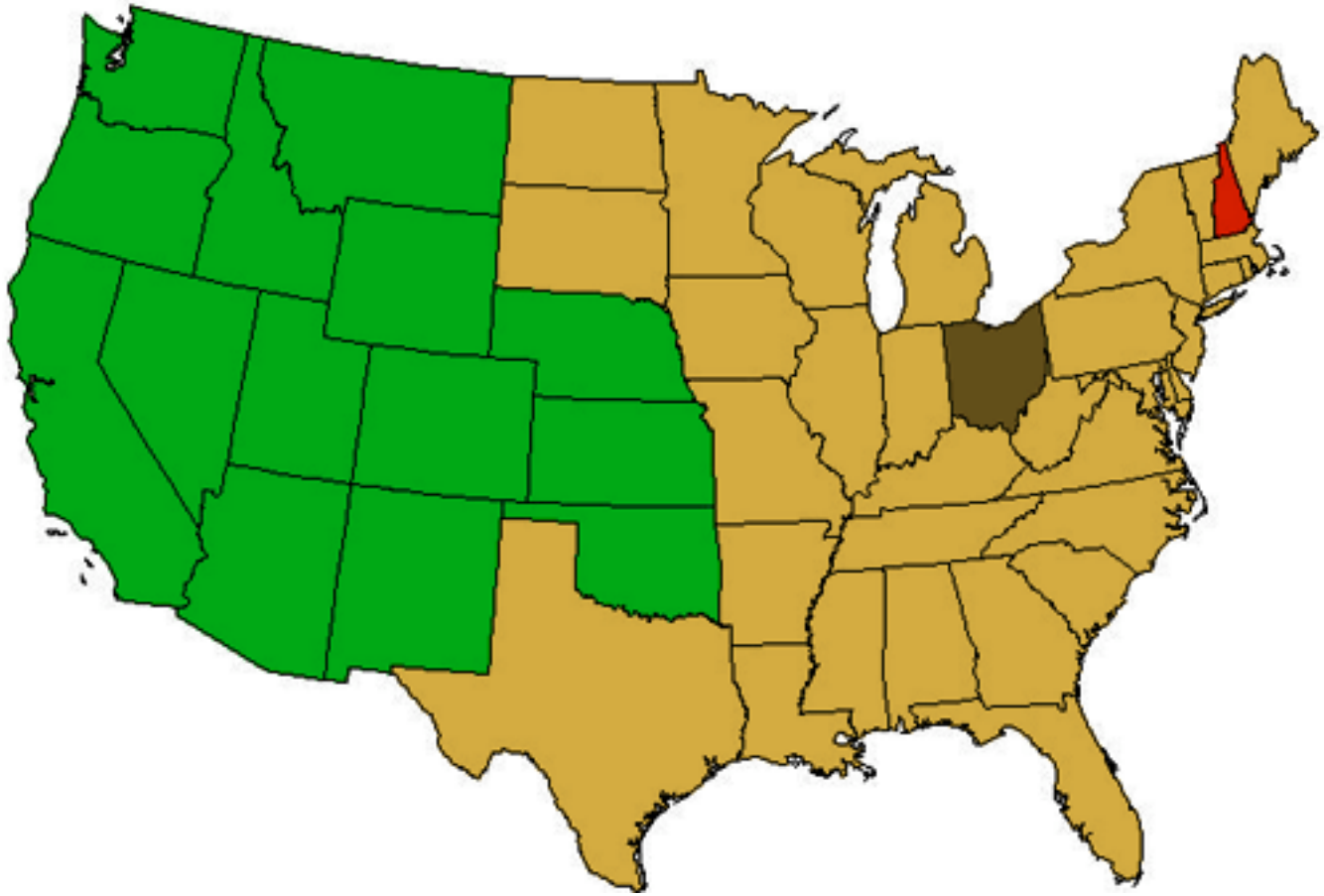
Jones seminar

2009.02.13

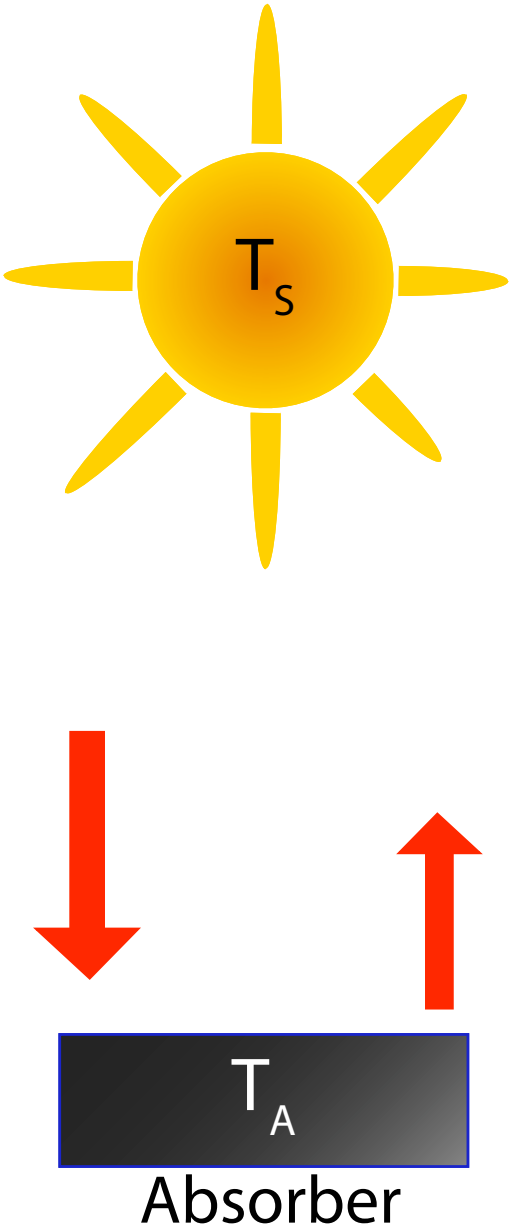


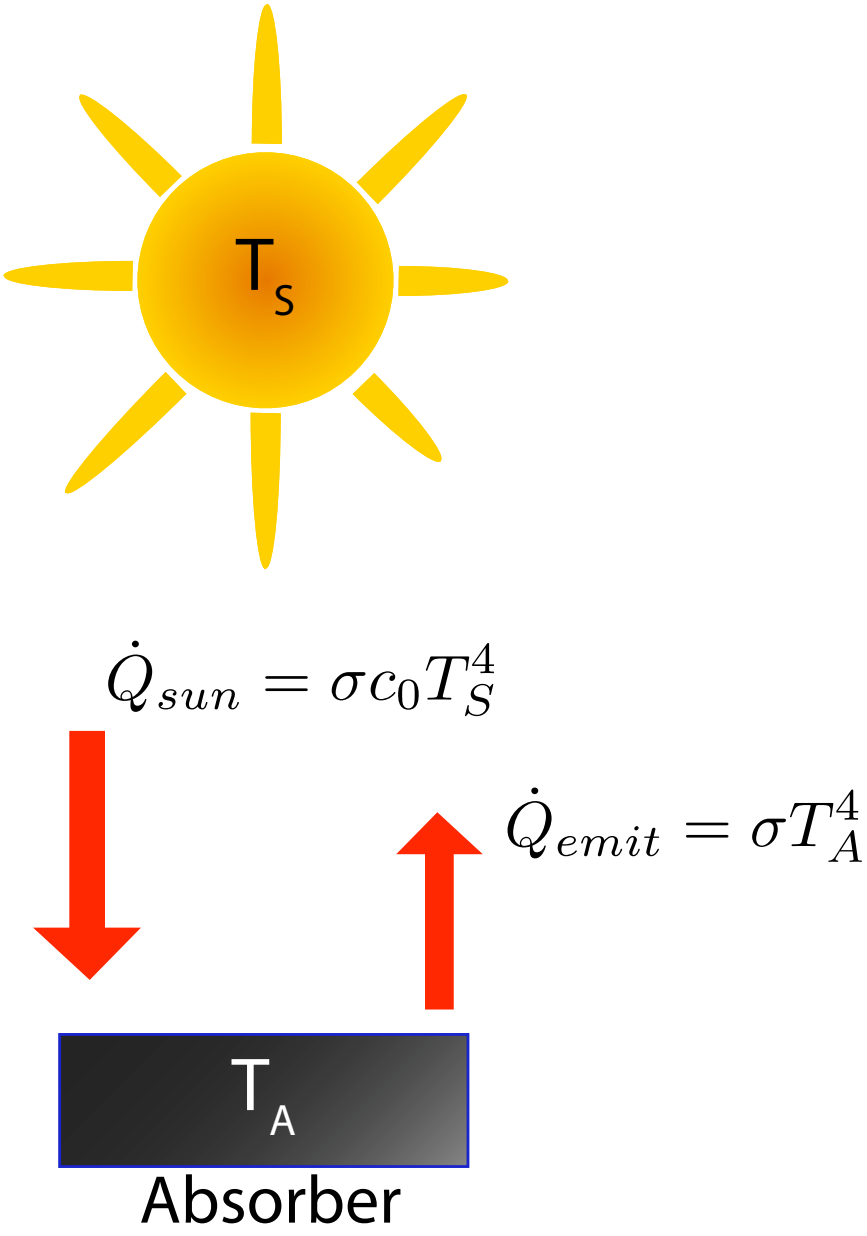
$$\frac{P_{sun}}{P_{people}} \approx 10^4$$

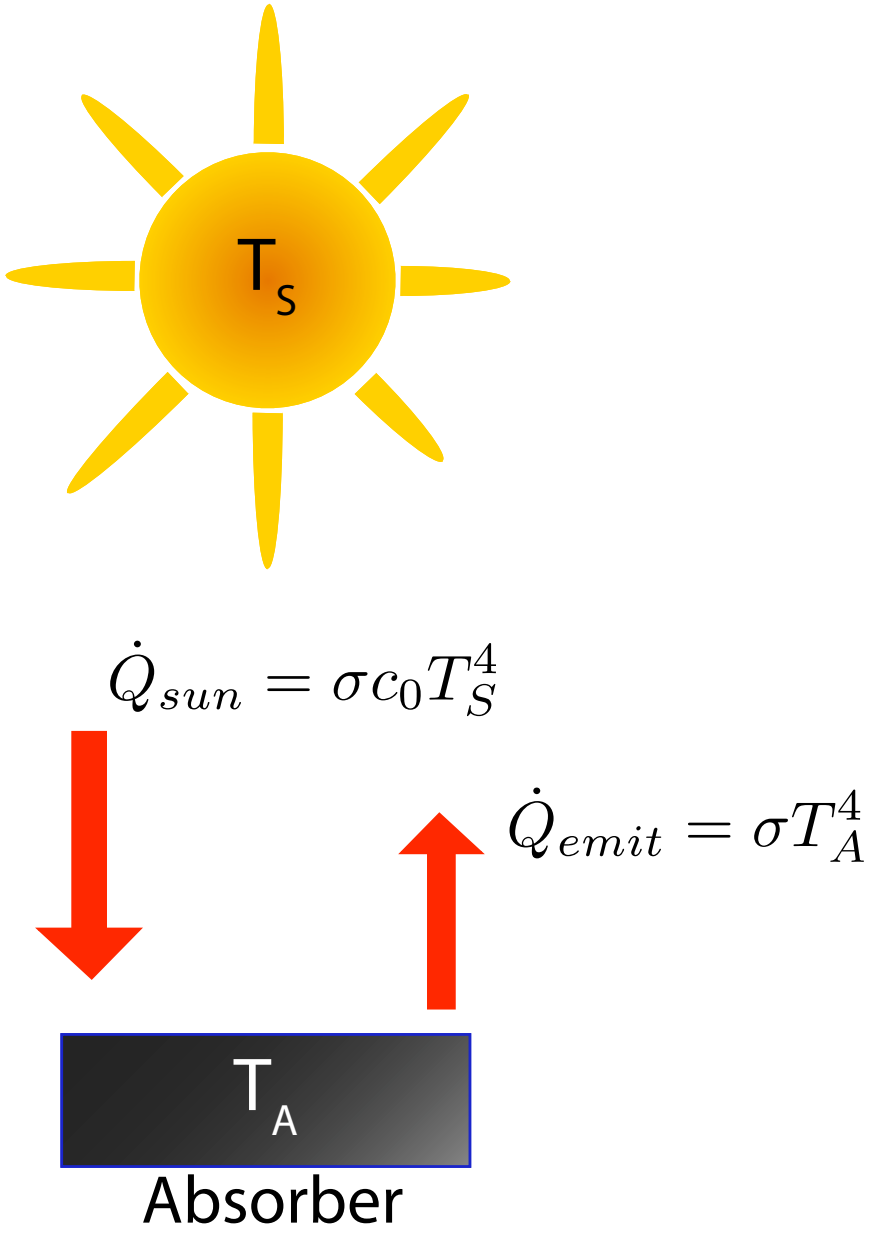




$$\frac{P_{sun}}{P_{people}} \approx 10^4$$

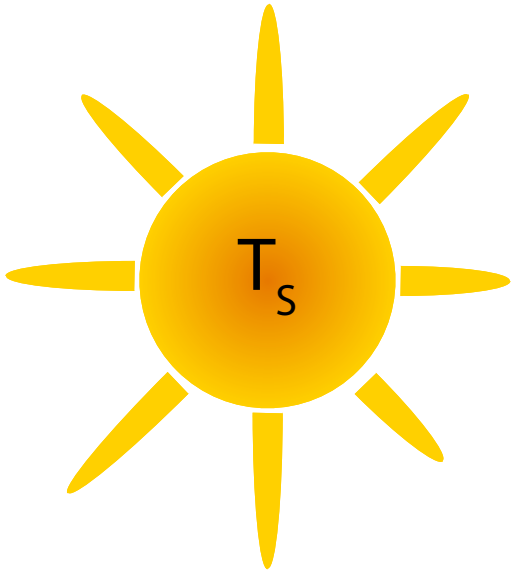

T_S
T_A
Absorber


T_S
$\dot{Q}_{sun} = \sigma c_0 T_S^4$
$\dot{Q}_{emit} = \sigma T_A^4$
T_A
Absorber



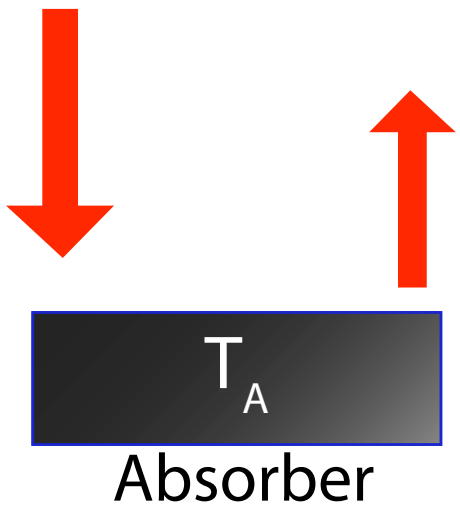
$$\dot{Q}_{emit} = \dot{Q}_{sun}$$

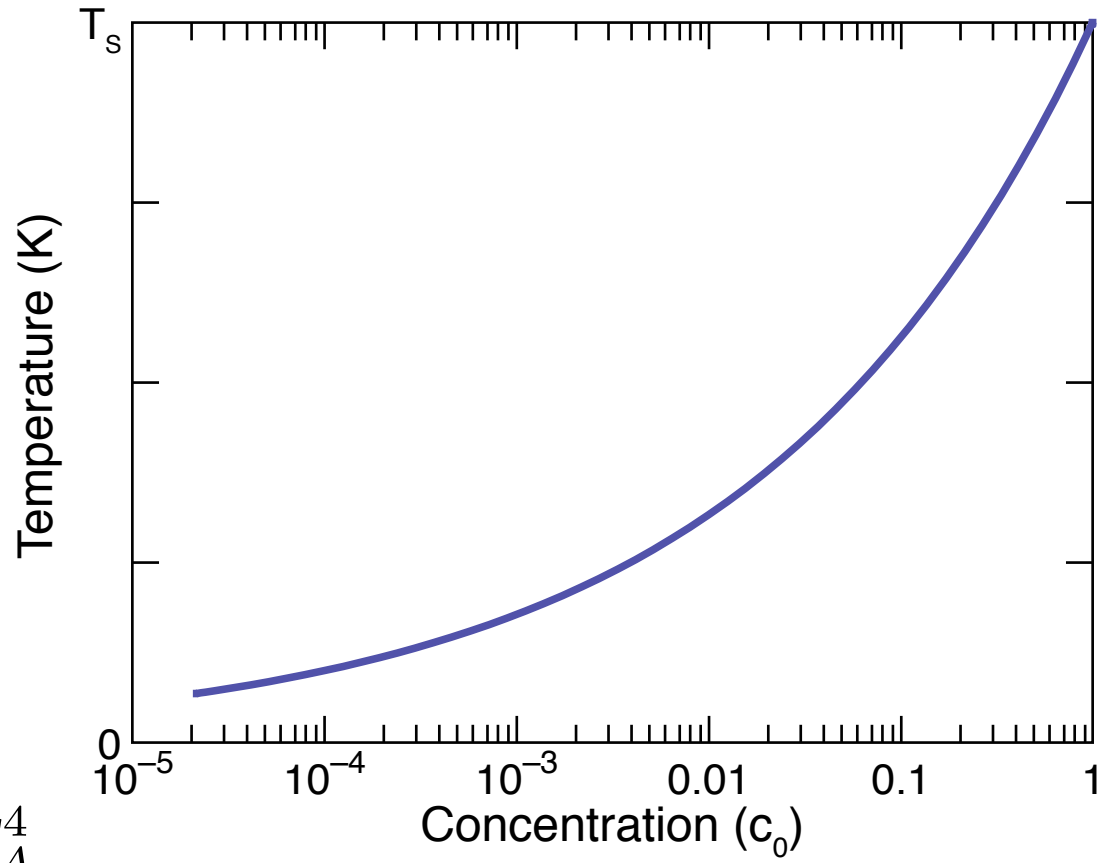
$$T_A = c_0^{\frac{1}{4}} T_S$$



$$\dot{Q}_{sun} = \sigma c_0 T_S^4$$

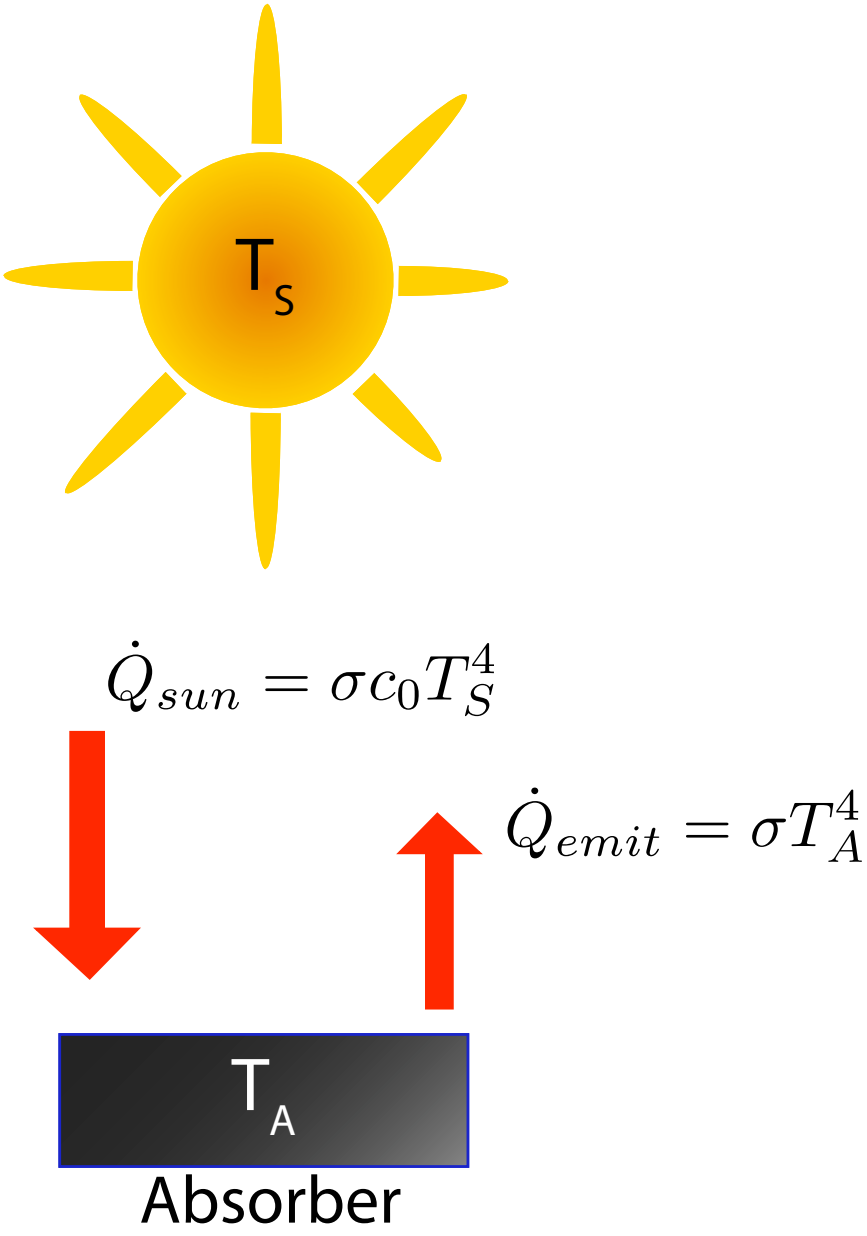
$$\dot{Q}_{emit} = \sigma T_A^4$$

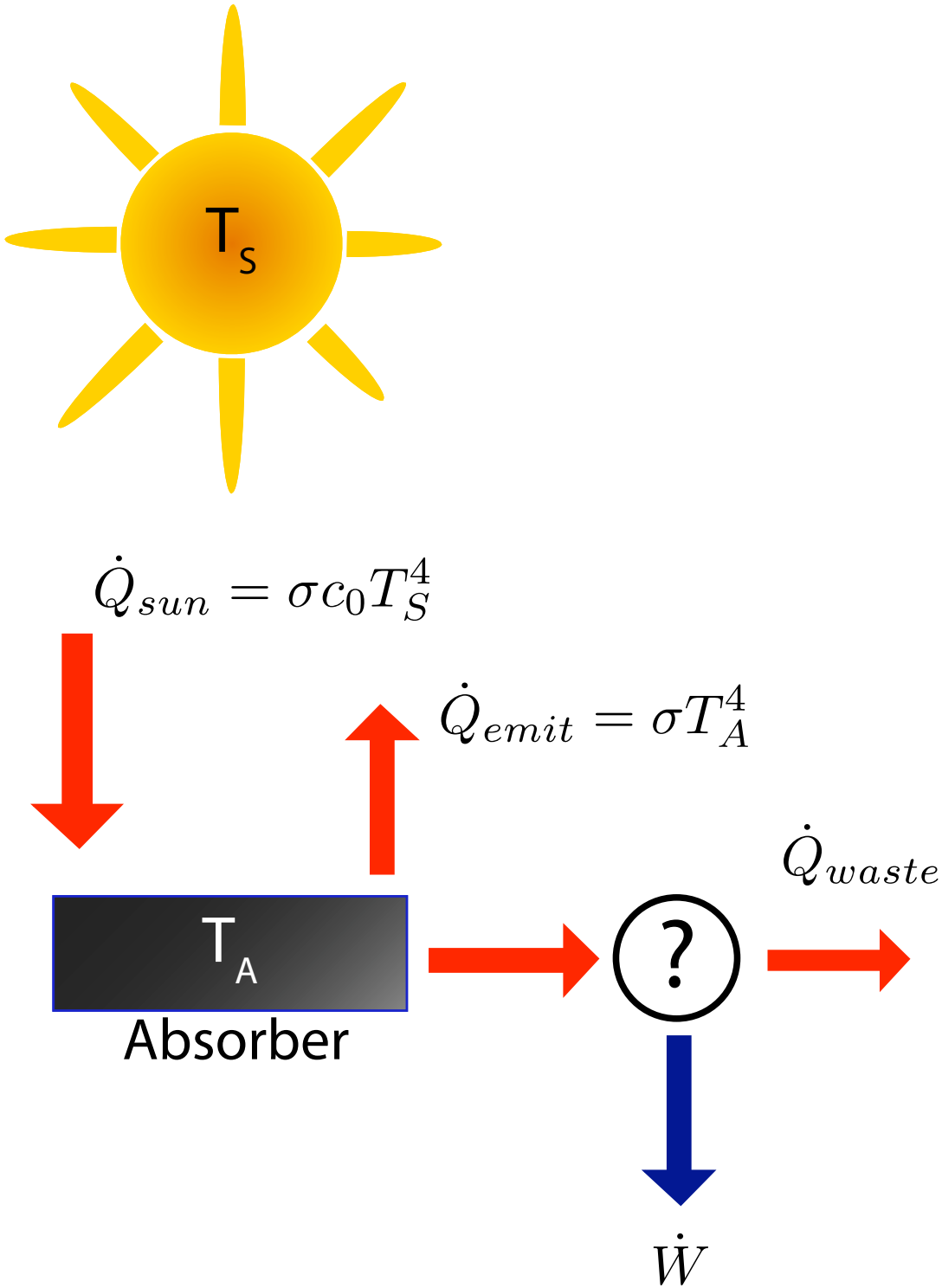


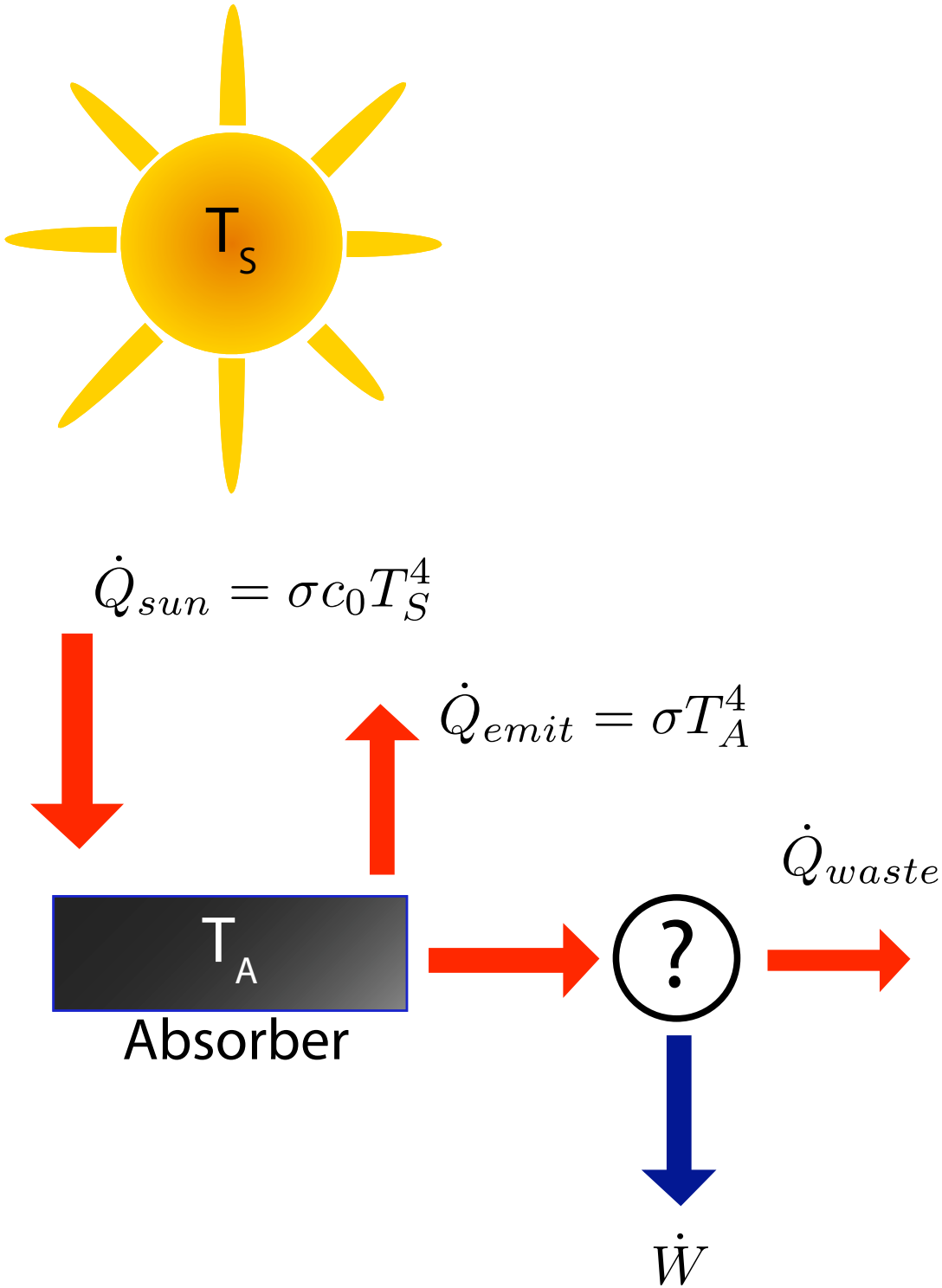


$$\dot{Q}_{emit} = \dot{Q}_{sun}$$

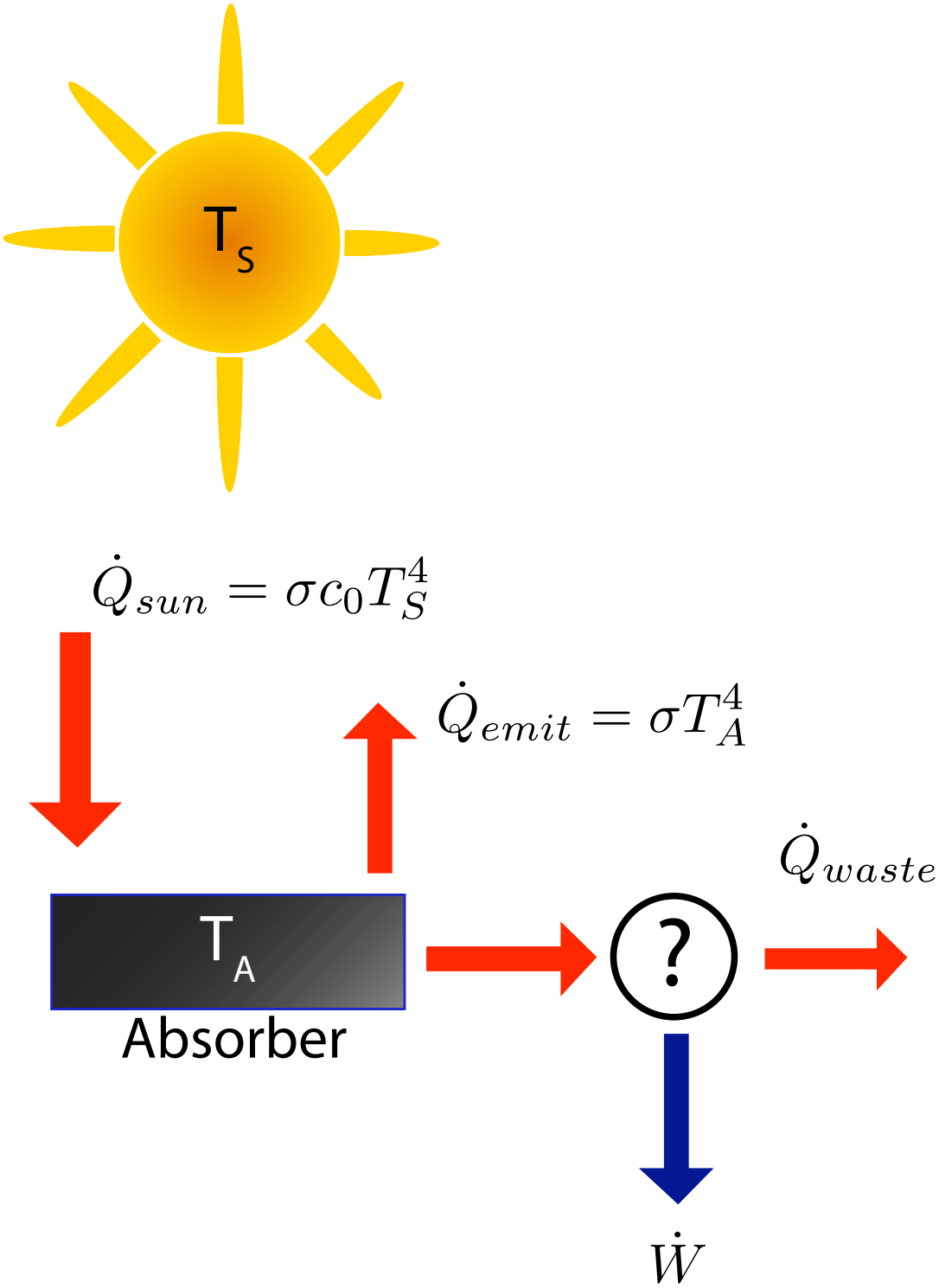
$$T_A = c_0^{\frac{1}{4}} T_S$$


T_S
$\dot{Q}_{sun} = \sigma c_0 T_S^4$
$\dot{Q}_{emit} = \sigma T_A^4$
T_A
Absorber


T_S
$\dot{Q}_{sun} = \sigma c_0 T_S^4$
$\dot{Q}_{emit} = \sigma T_A^4$
$\dot{Q}_{waste}$
T_A
Absorber
?
$\dot{W}$

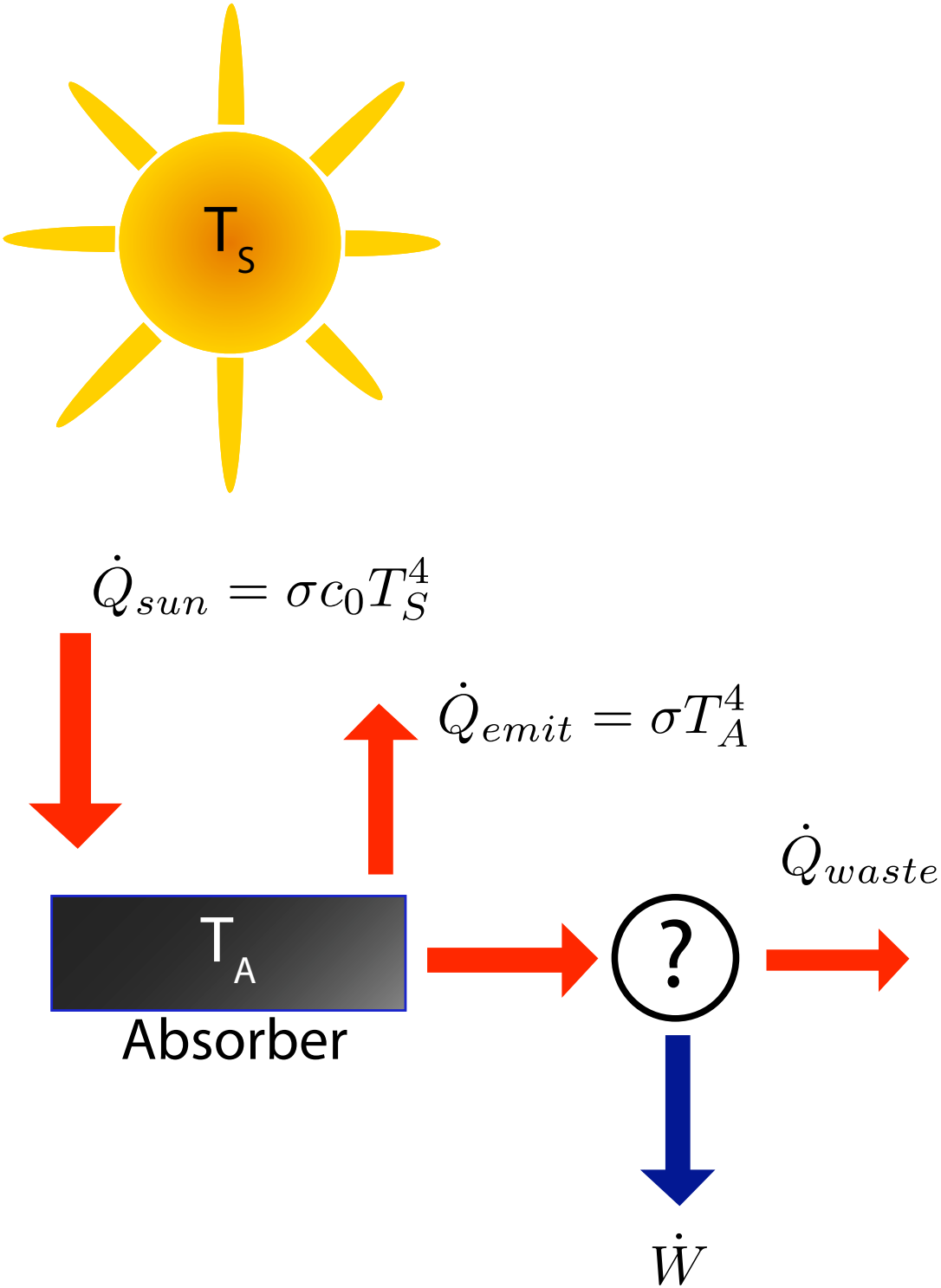


$$\eta = \frac{\dot{W}}{\dot{Q}_{sun}}$$



$$\eta = \frac{\dot{W}}{\dot{Q}_{sun}}$$

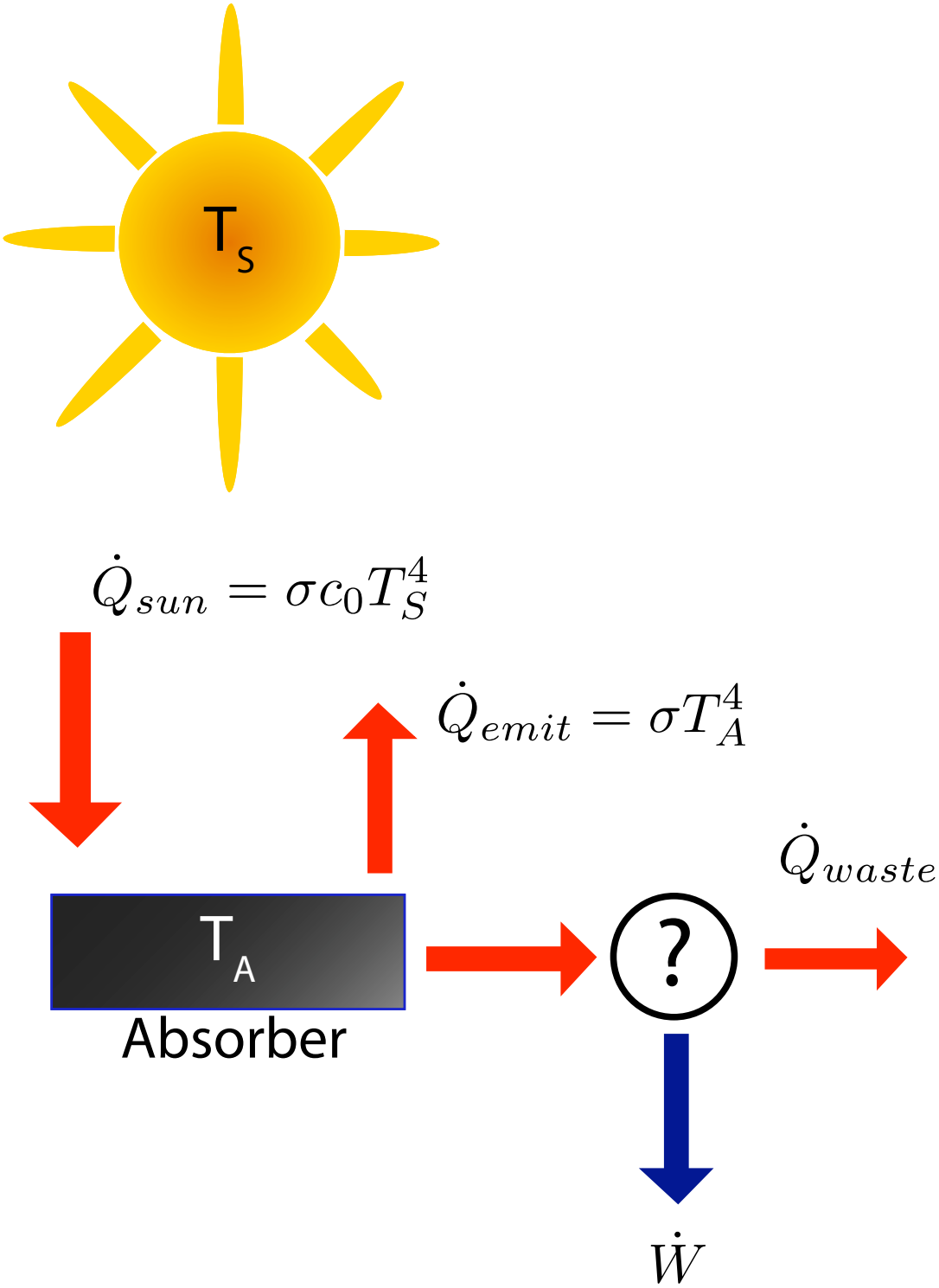
$$\eta = \frac{\dot{Q}_{sun} - \dot{Q}_{emit} - \dot{Q}_{waste}}{\dot{Q}_{sun}}$$



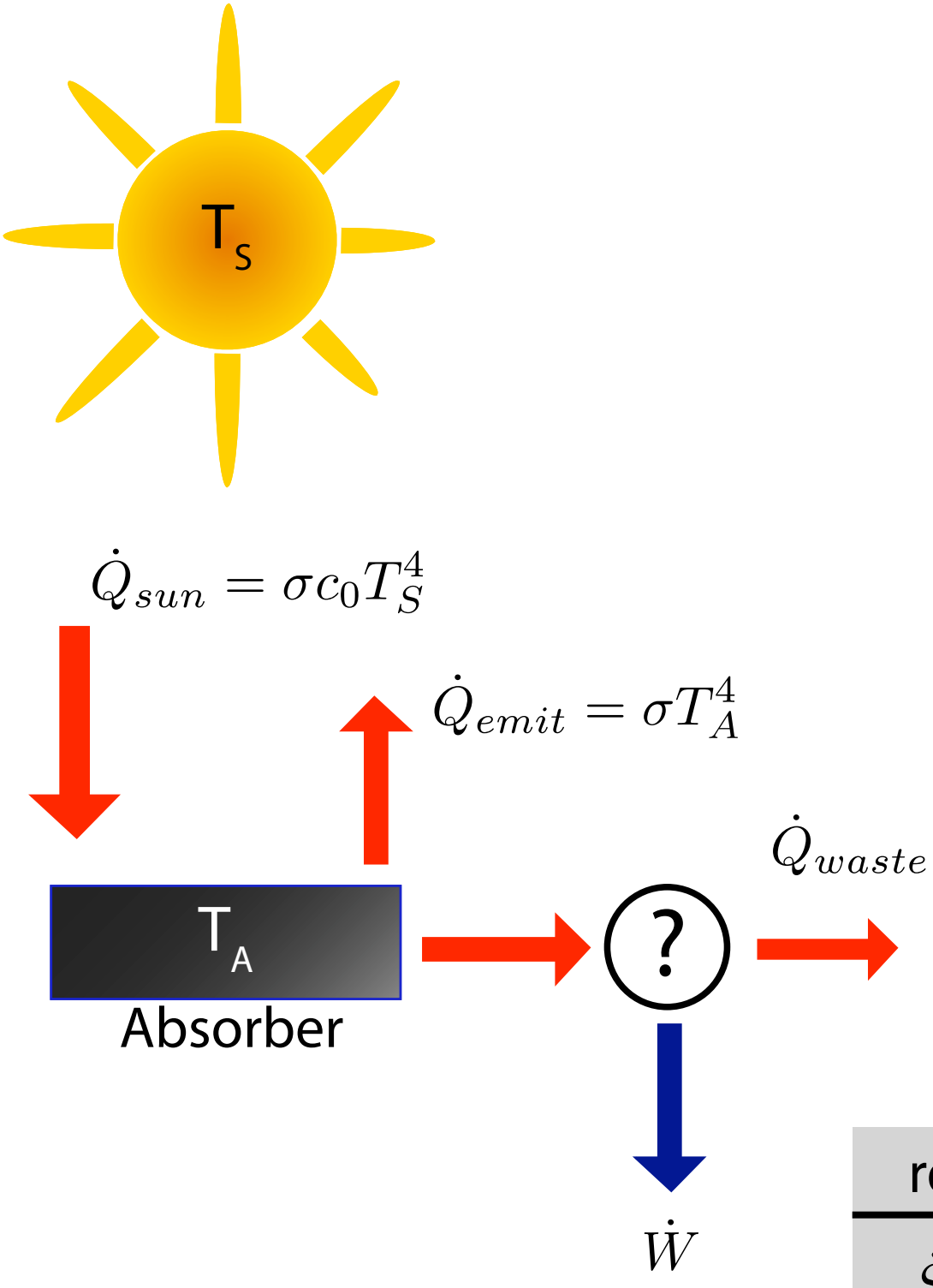
$$\eta = \frac{\dot{W}}{\dot{Q}_{sun}}$$

$$\eta = \frac{\dot{Q}_{sun} - \dot{Q}_{emit} - \dot{Q}_{waste}}{\dot{Q}_{sun}}$$

$$\eta = 1 - \left(\frac{T_A}{c_0 T_S}\right)^4 - \frac{\dot{Q}_{waste}}{c_0 \sigma T_S^4}$$

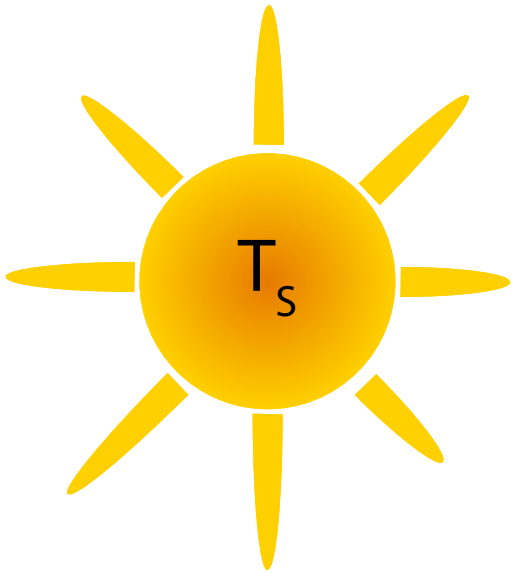


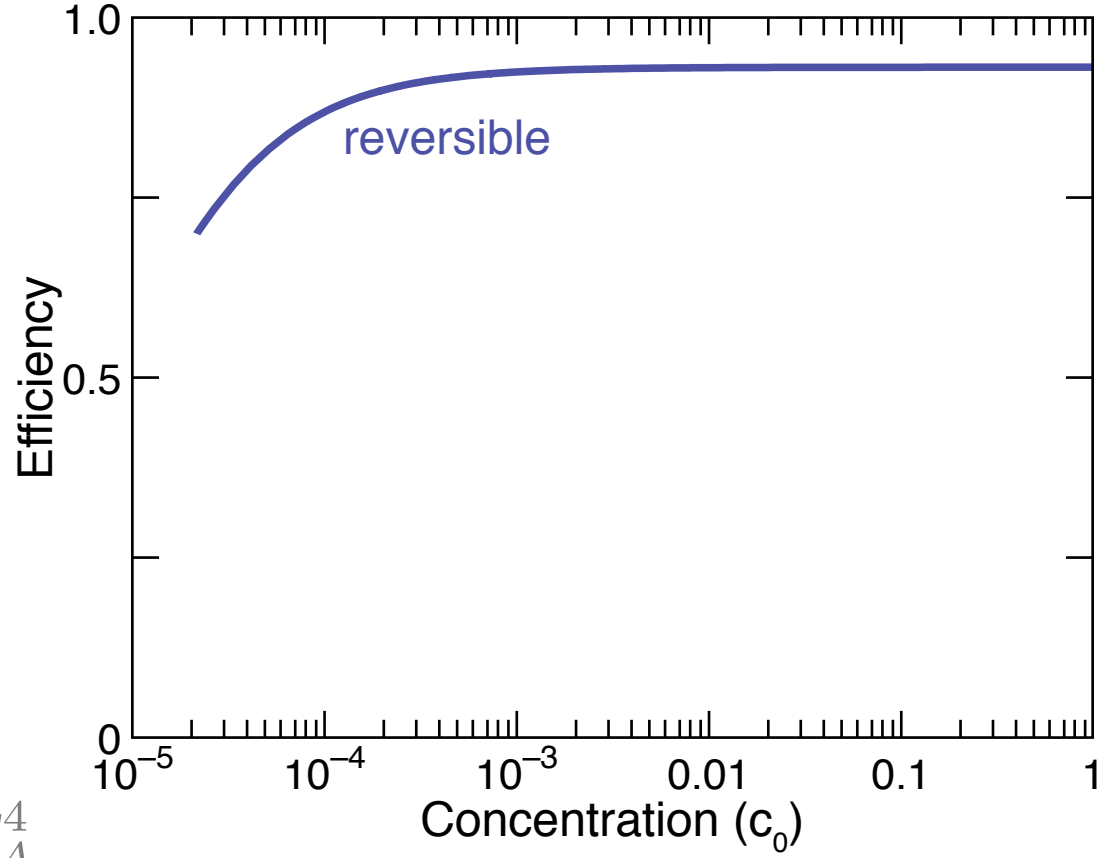
$$\eta = 1 - \left(\frac{T_A}{c_0 T_S}\right)^4 - \frac{\dot{Q}_{waste}}{c_0 \sigma T_S^4}$$

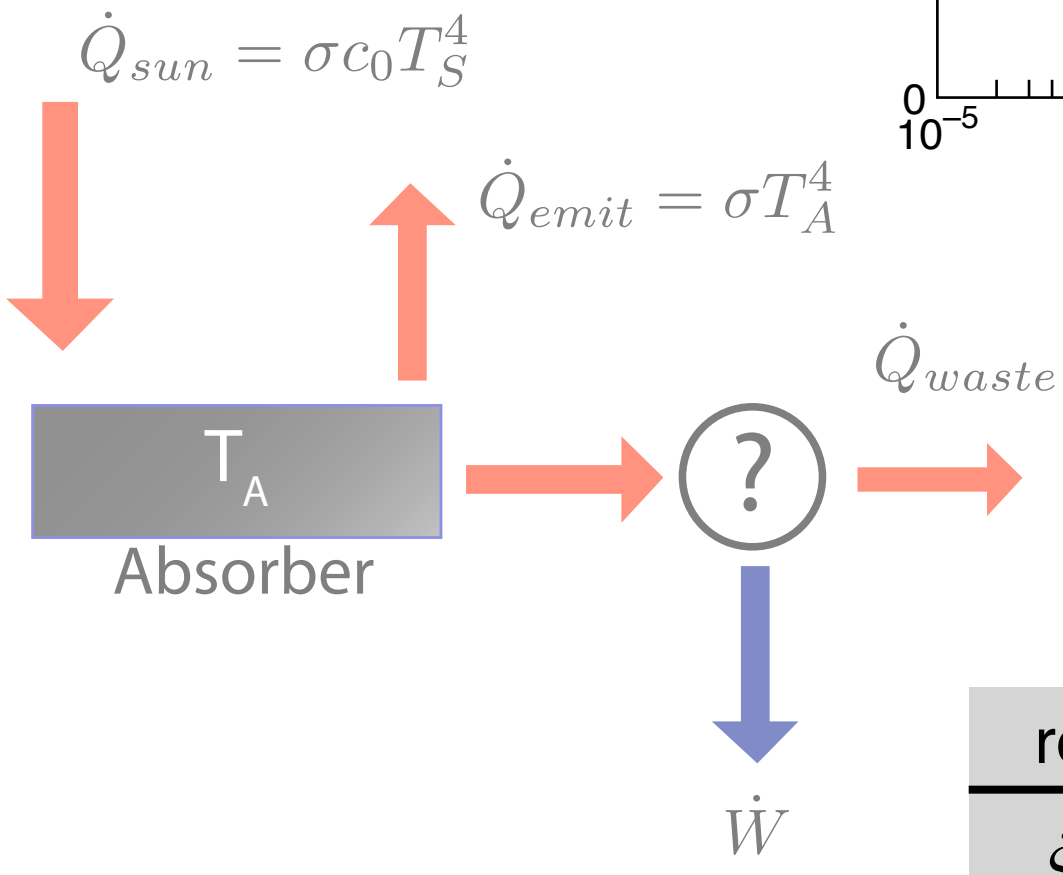


$$\eta = 1 - \left(\frac{T_A}{c_0 T_S}\right)^4 - \frac{\dot{Q}_{waste}}{c_0 \sigma T_S^4}$$

reversible
$\dot{S}_{tot} = \dot{S}_{sun} - \dot{S}_{emit} - \dot{S}_{waste} = 0$



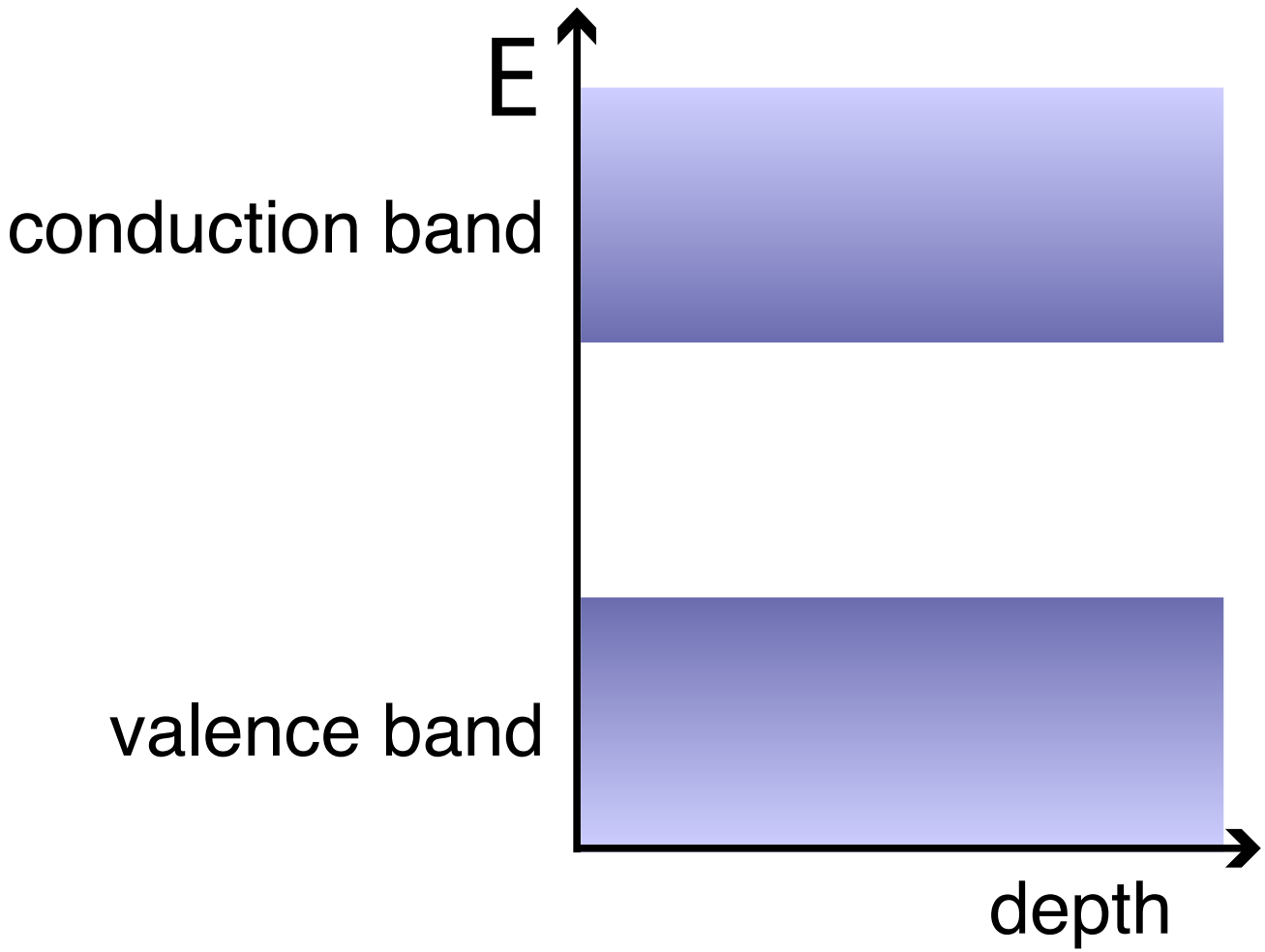


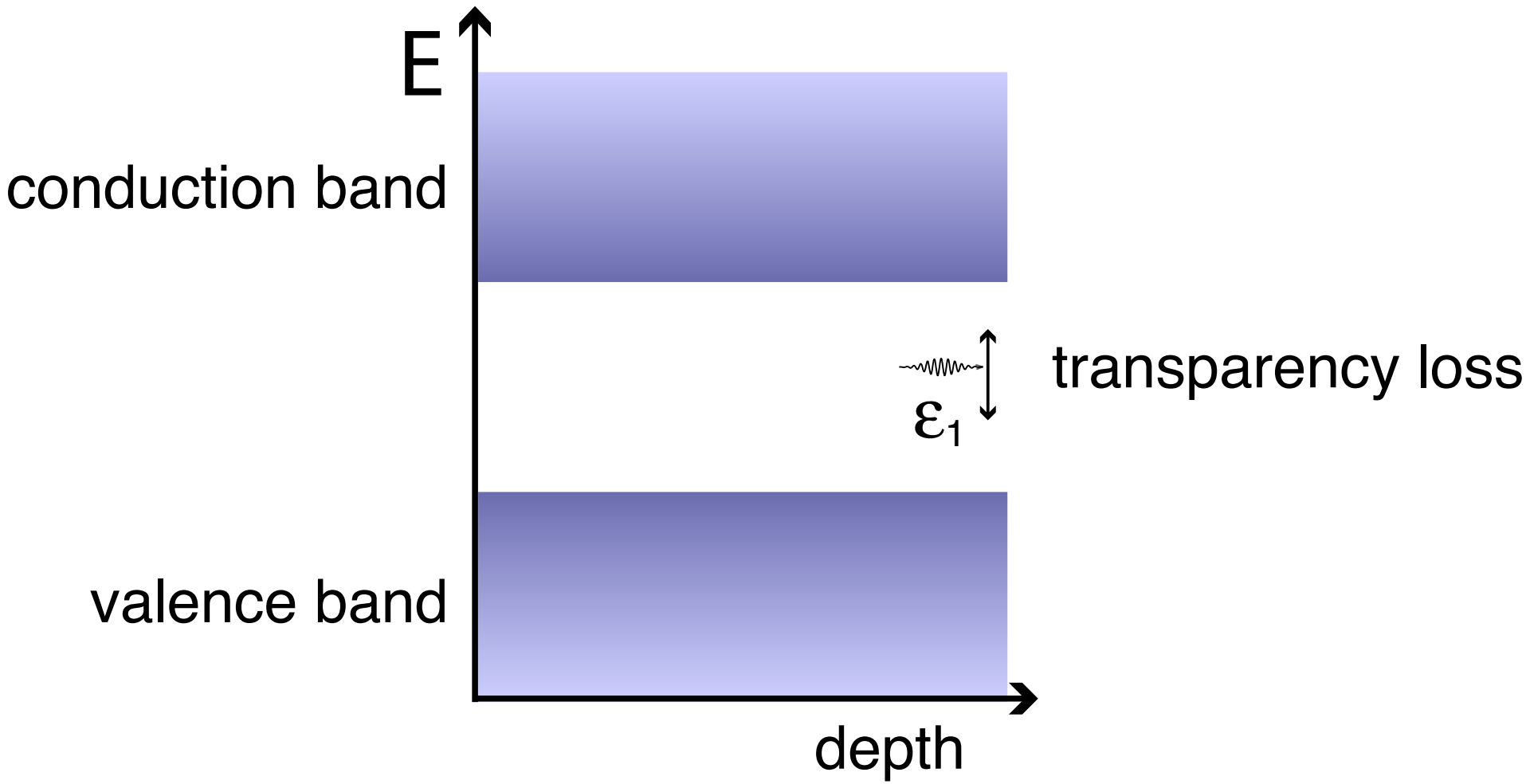


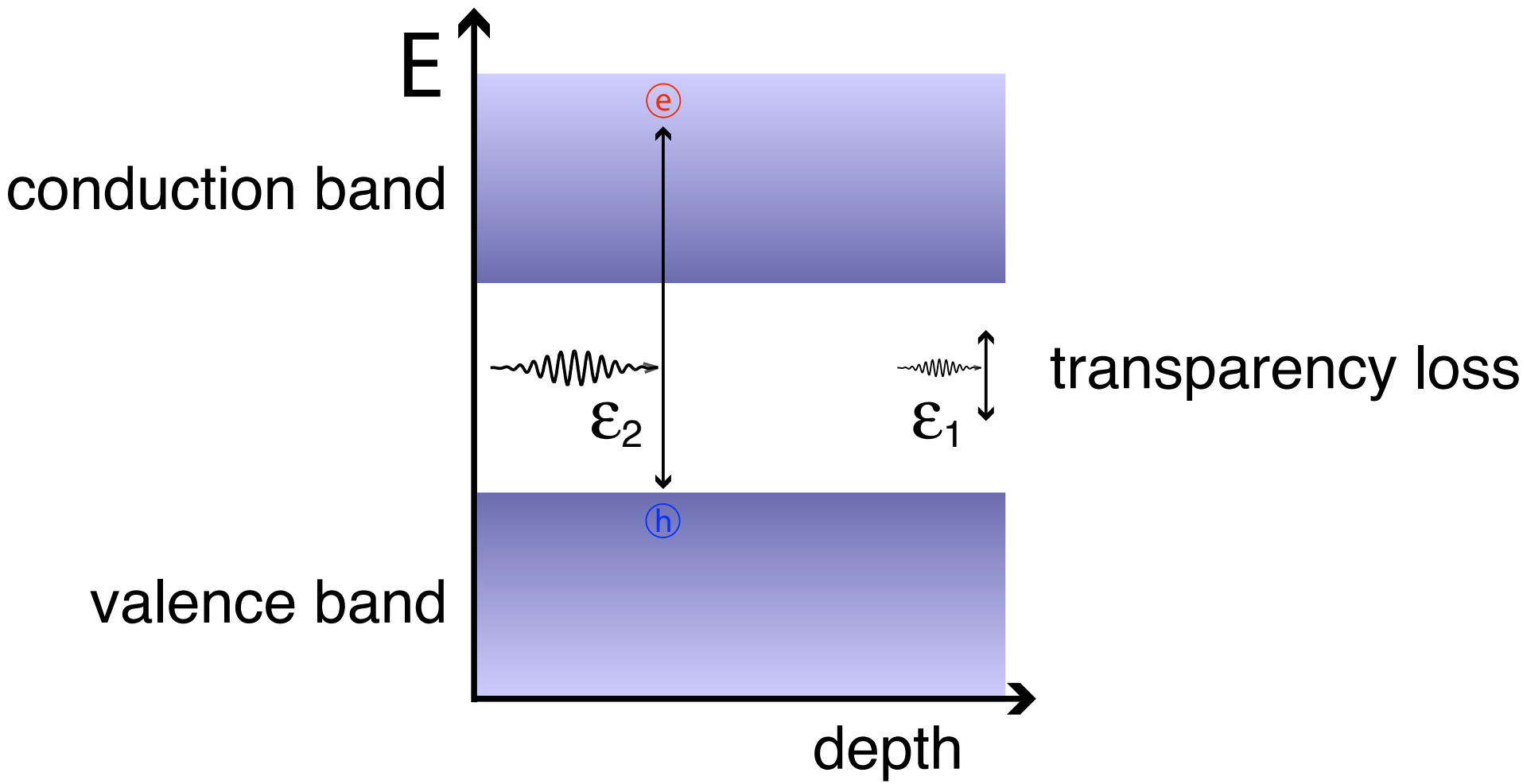
$$\eta = 1 - \left(\frac{T_A}{c_0 T_S}\right)^4 - \frac{\dot{Q}_{waste}}{c_0 \sigma T_S^4}$$

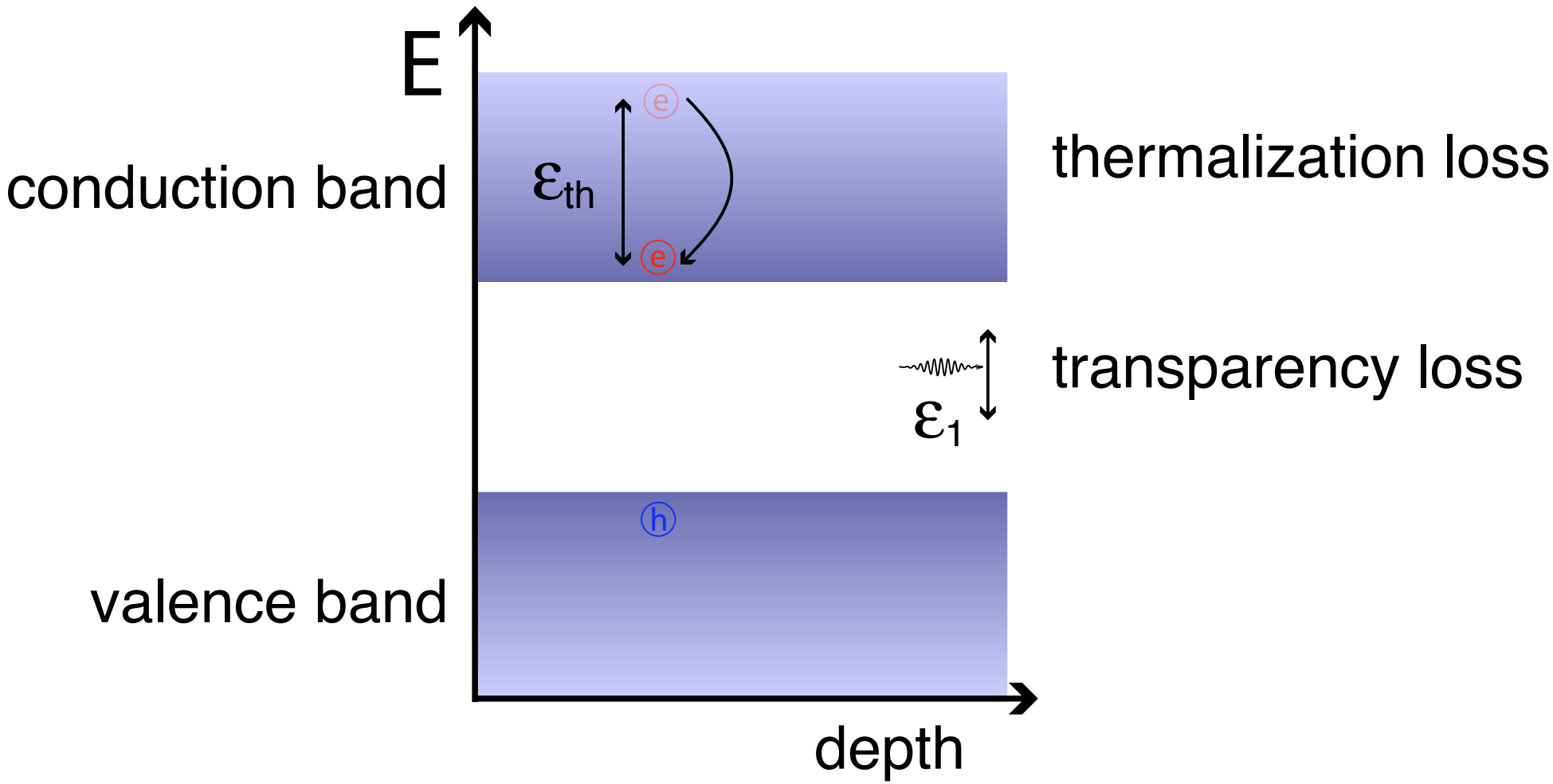
reversible

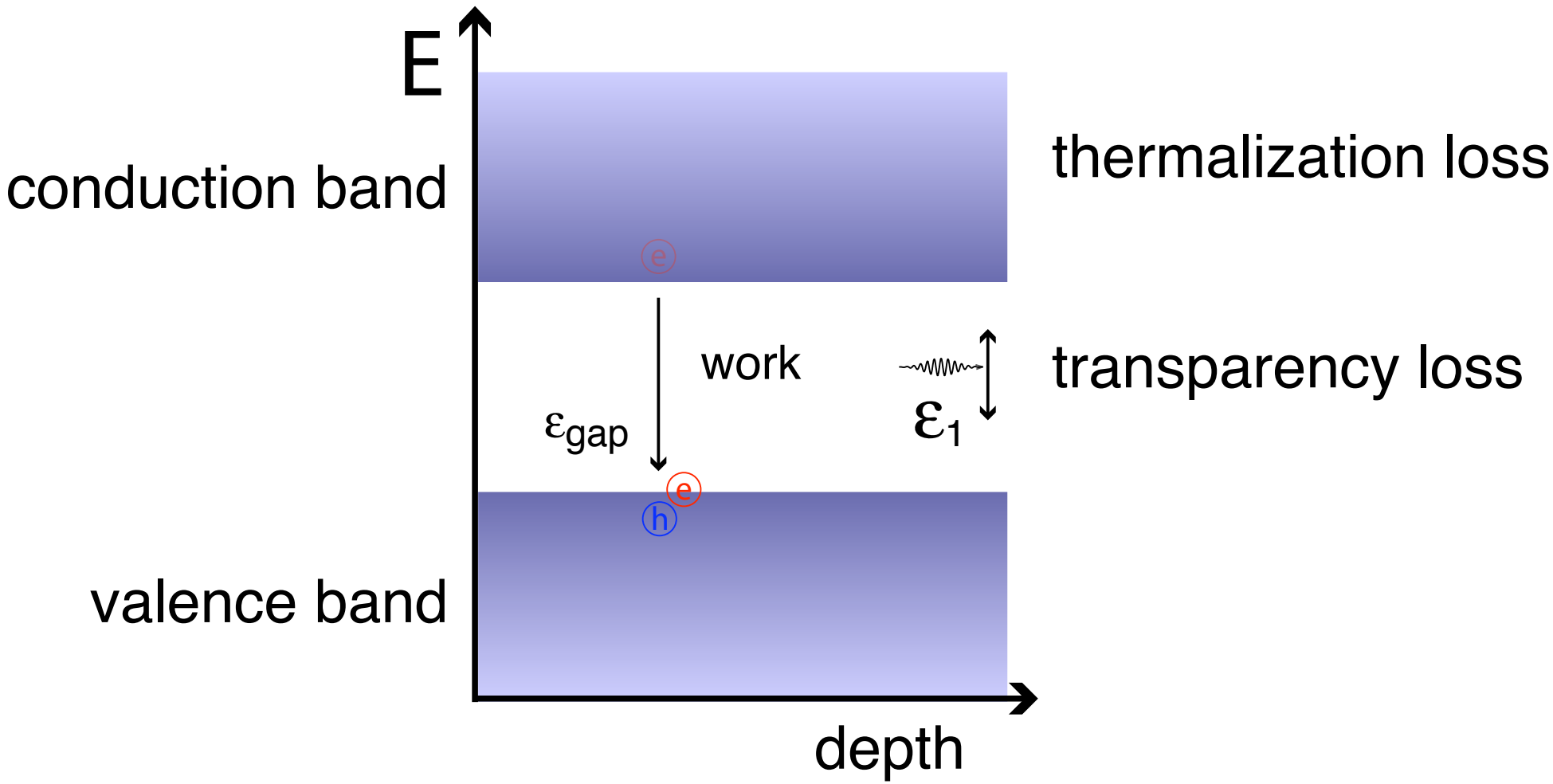
$$\dot{S}_{tot} = \dot{S}_{sun} - \dot{S}_{emit} - \dot{S}_{waste} = 0$$

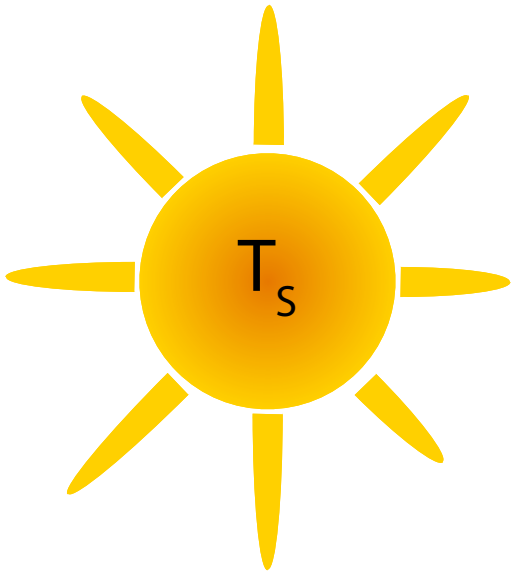

E
conduction band
valence band
depth

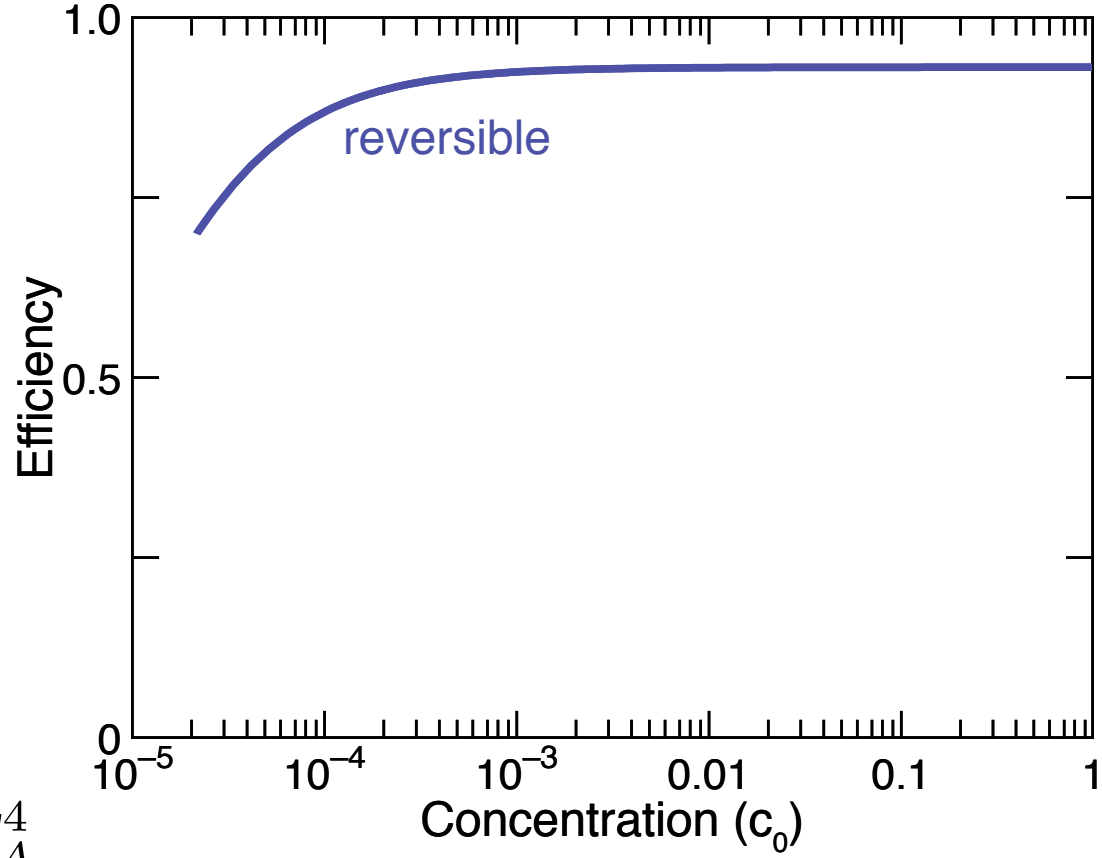

E
conduction band
transparency loss
ε_1
valence band
depth


E
conduction band
e
ε_2
ε_1
transparency loss
h
valence band
depth


E
conduction band
ε_{th}
e
e
thermalization loss
transparency loss
ε_1
h
valence band
depth


E
conduction band
thermalization loss
e
work
transparency loss
ε_{gap}
ε_1
e
h
valence band
depth

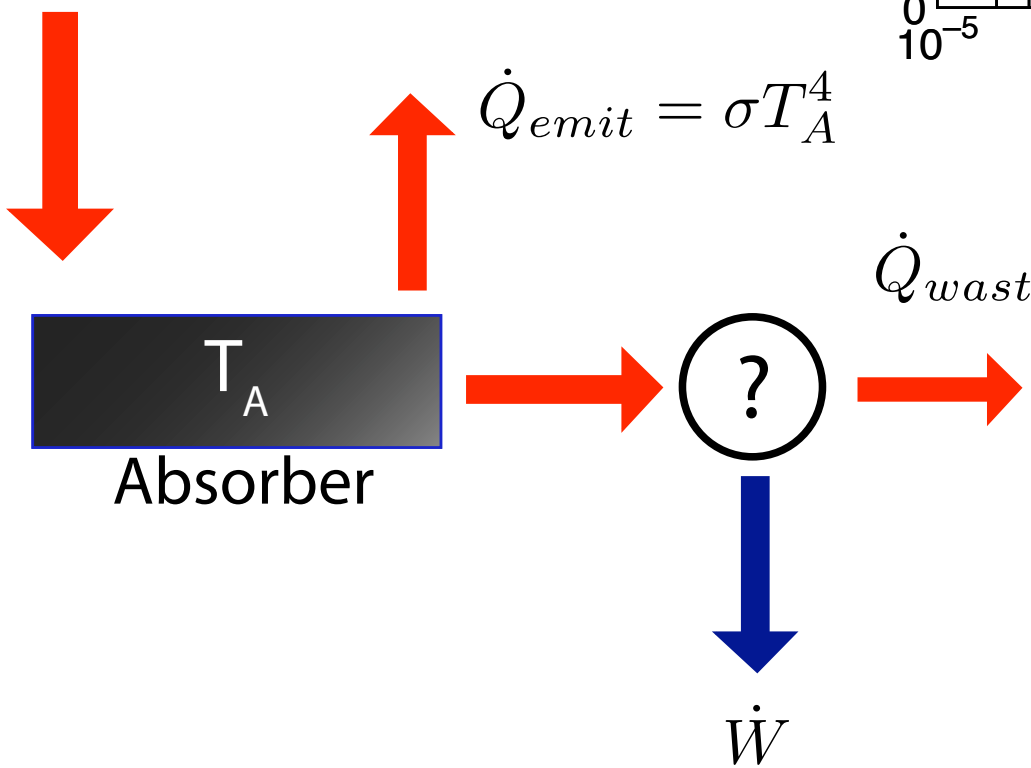




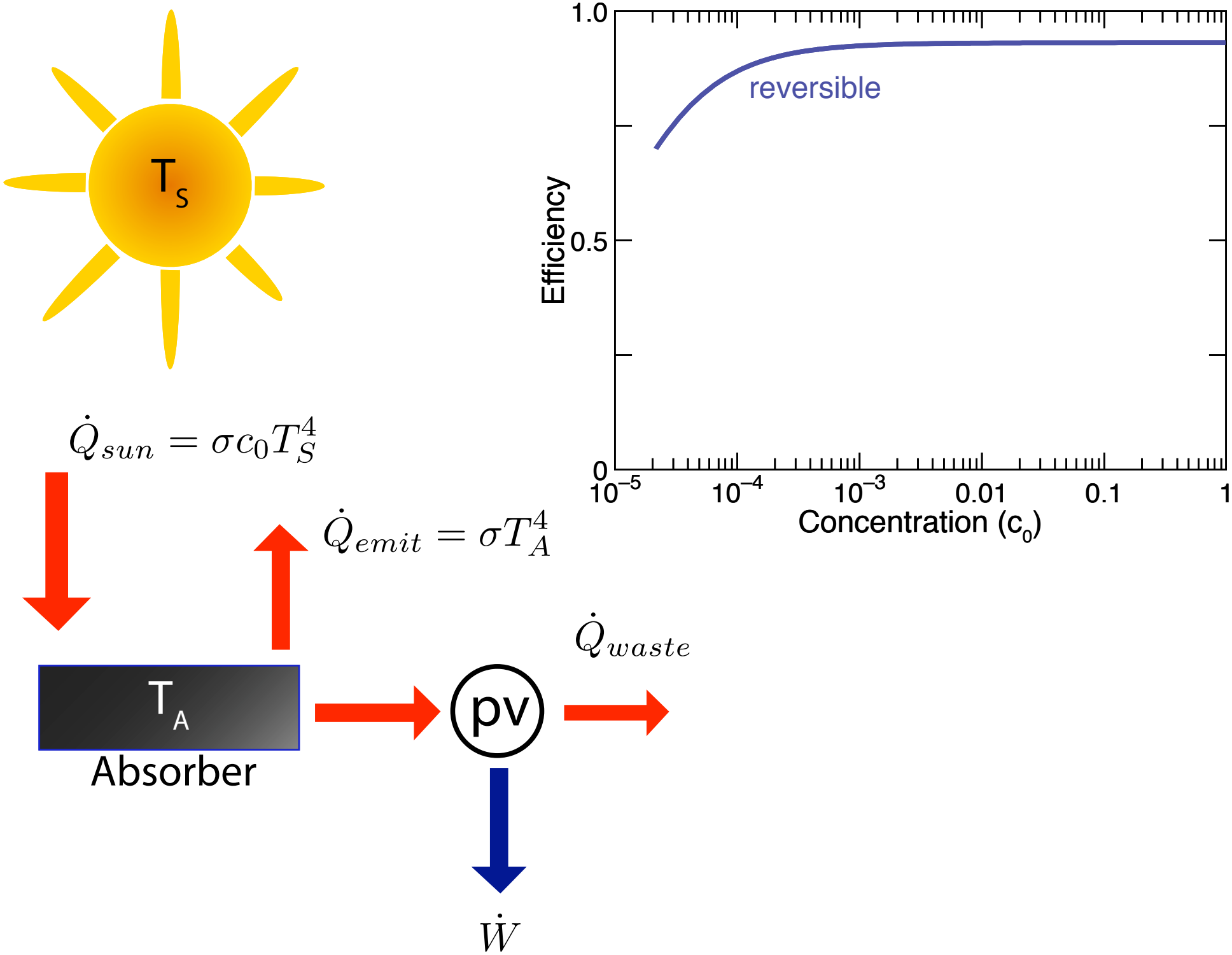
$$\dot{Q}_{sun} = \sigma c_0 T_S^4$$

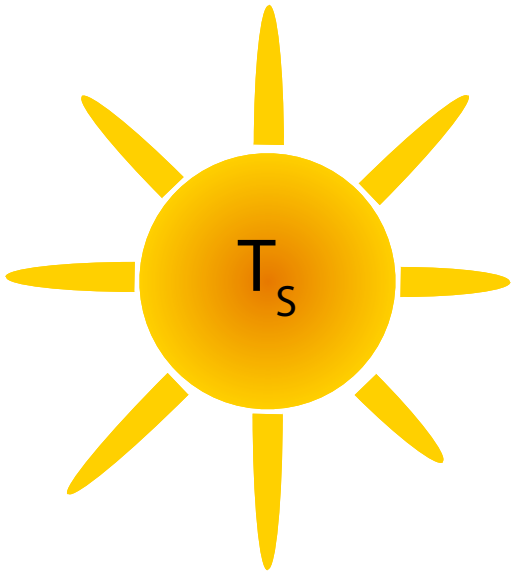
$$\dot{Q}_{emit} = \sigma T_A^4$$

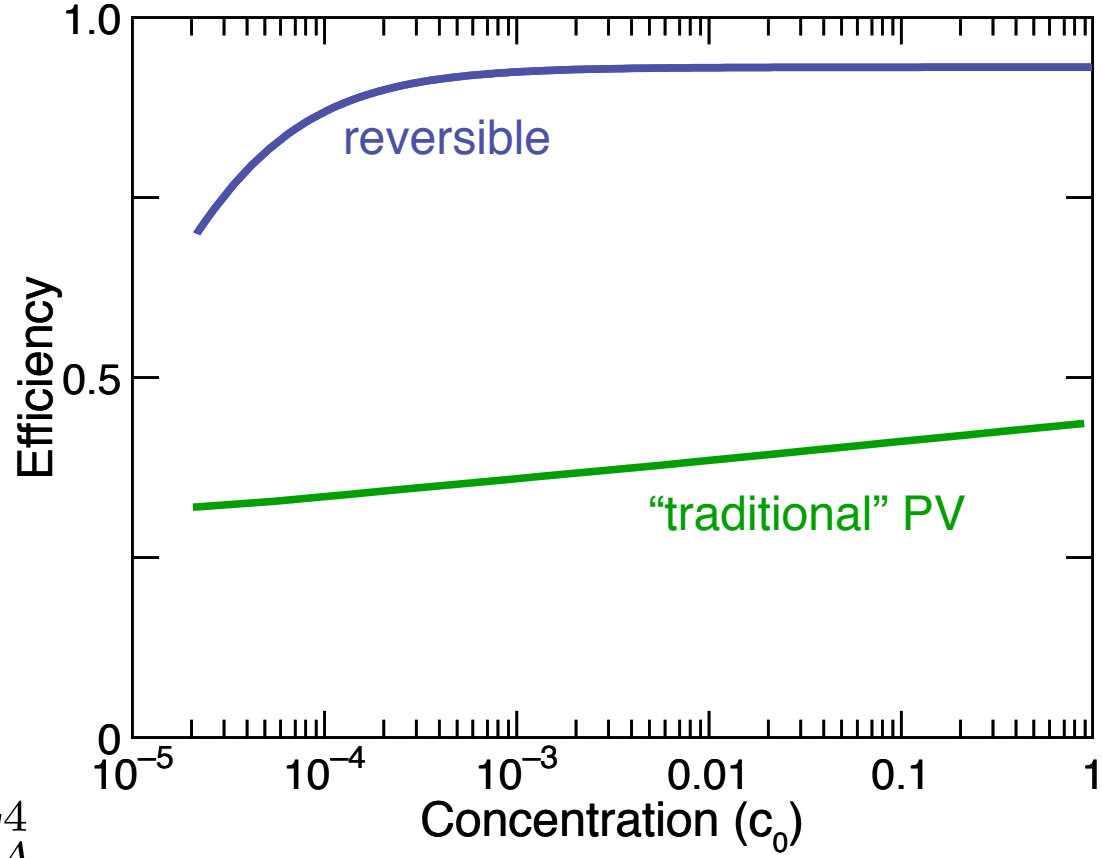
$$\dot{Q}_{waste}$$

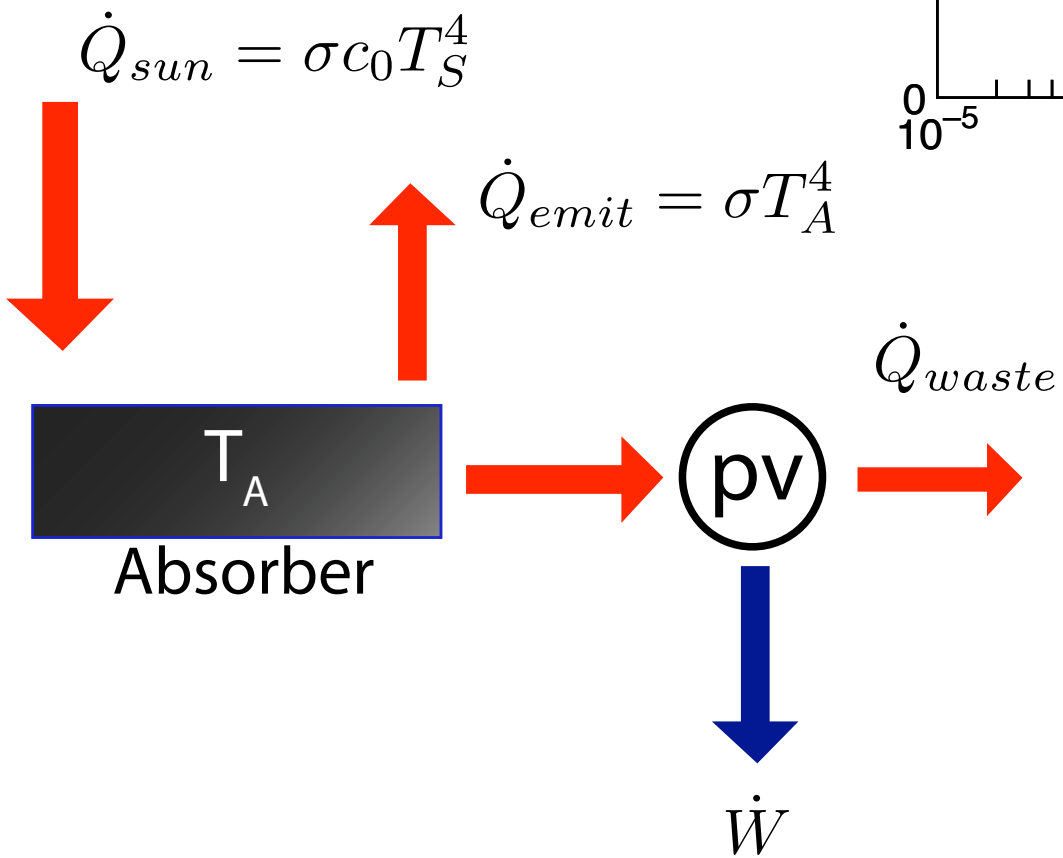


$$\dot{W}$$

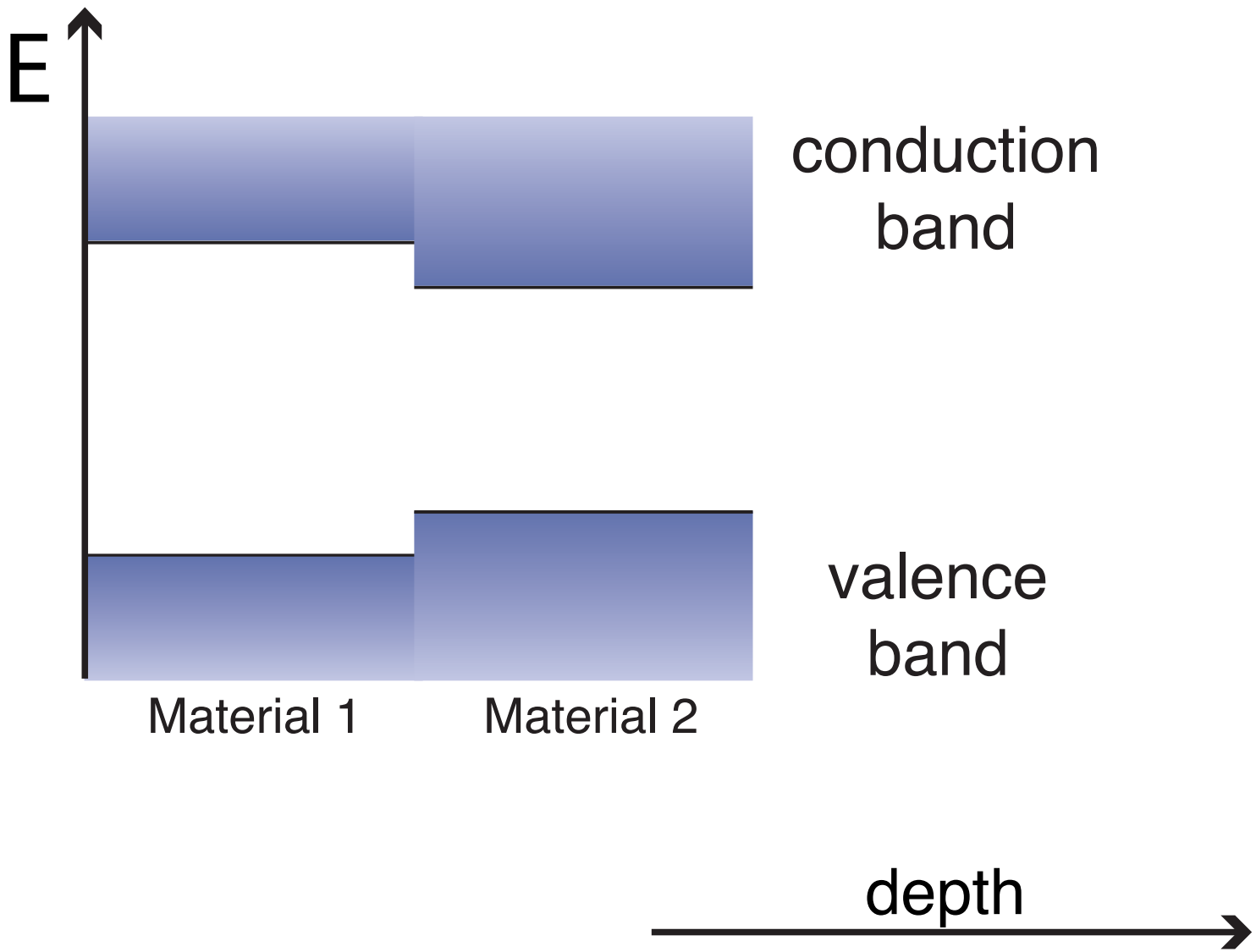

T_S
$\dot{Q}_{sun} = \sigma c_0 T_S^4$
$\dot{Q}_{emit} = \sigma T_A^4$
T_A
Absorber
pv
$\dot{Q}_{waste}$
$\dot{W}$
1.0
0.5
0
Efficiency
reversible
10^{-5}
10^{-4}
10^{-3}
0.01
0.1
1
Concentration (c_0)


T
S

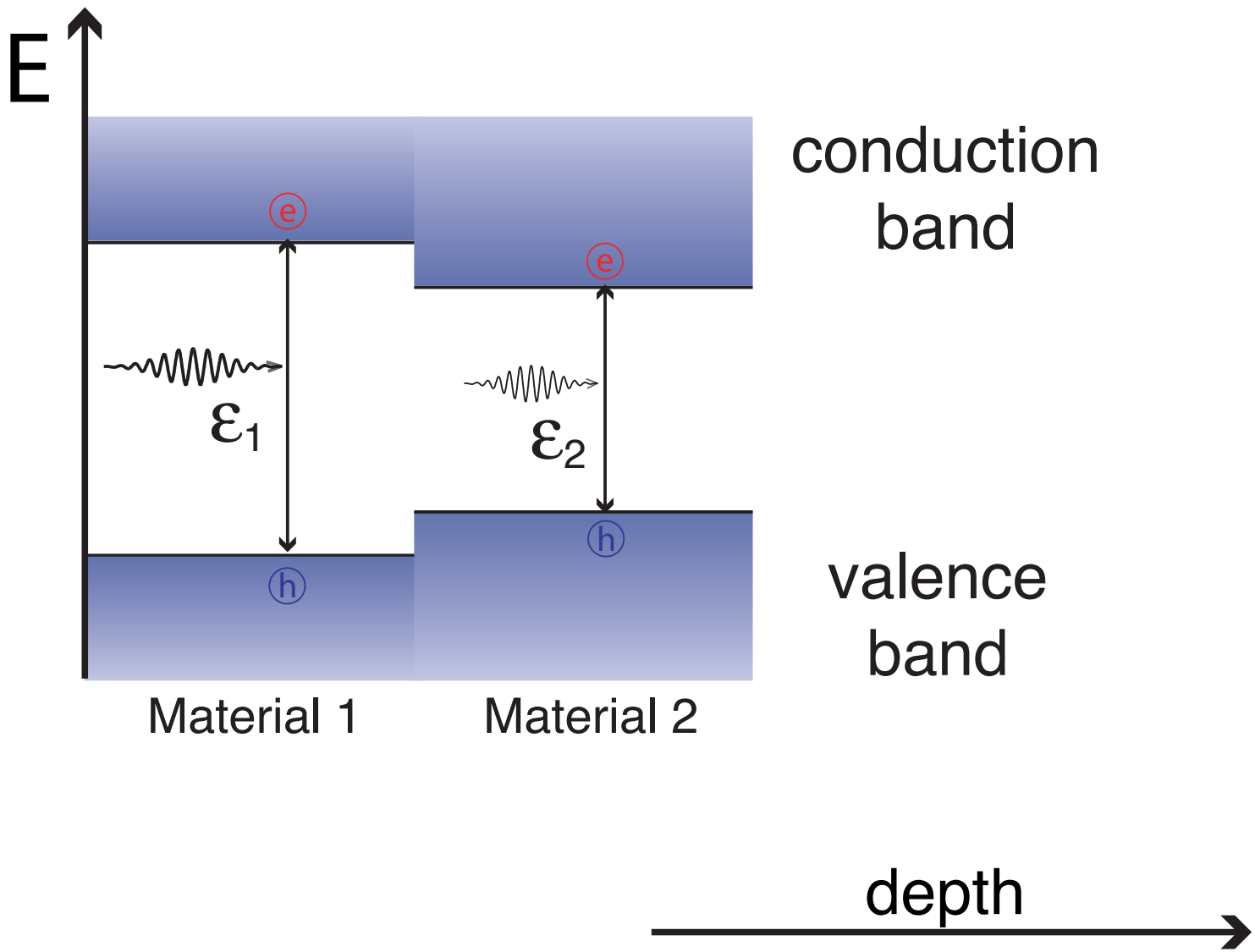

1.0
0.5
0
Efficiency
reversible
"traditional" PV
10^{-5}
10^{-4}
10^{-3}
0.01
0.1
1
Concentration (c_0)

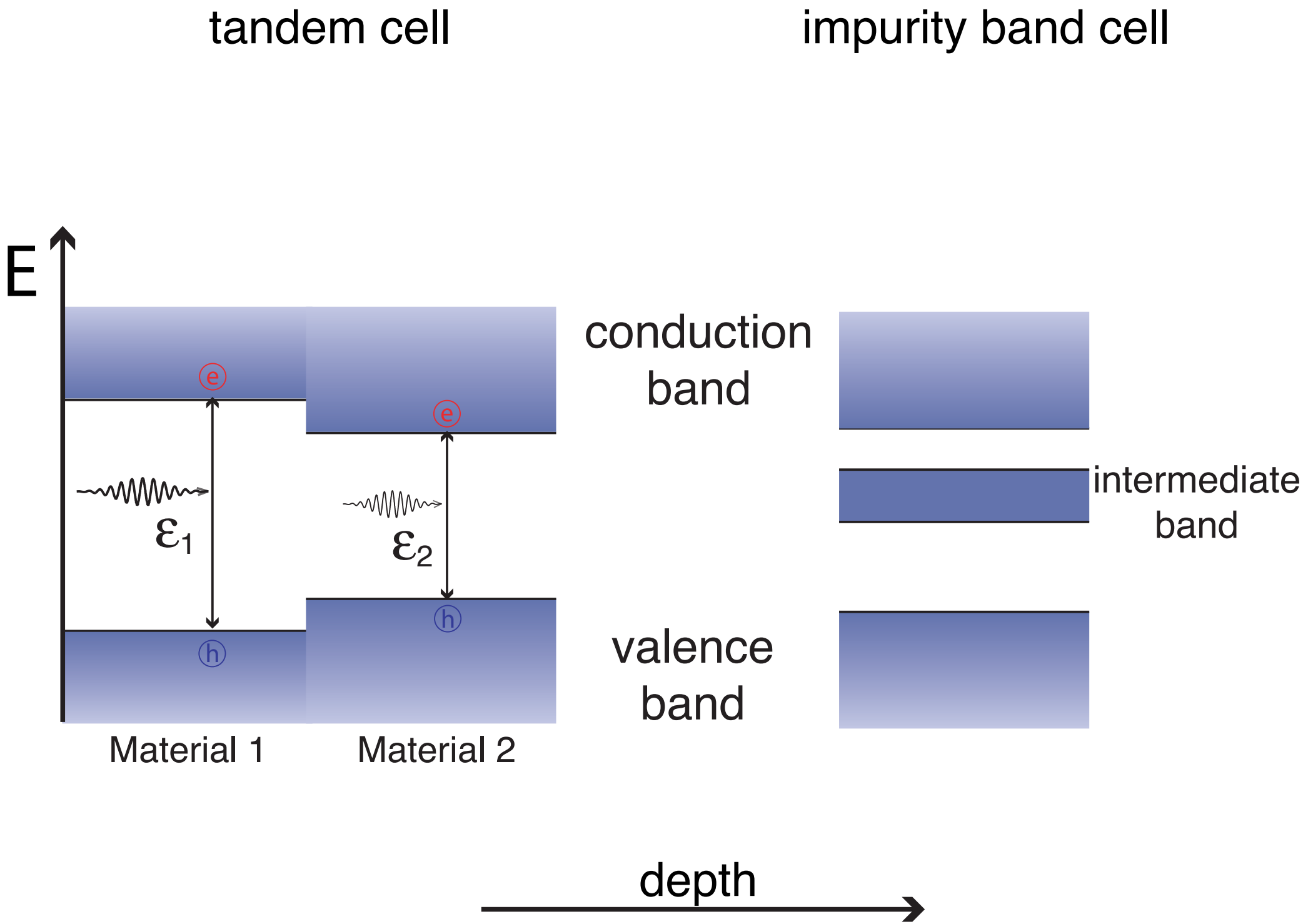

$\dot{Q}_{sun} = \sigma c_0 T_S^4$
$\dot{Q}_{emit} = \sigma T_A^4$
$\dot{Q}_{waste}$
T
A
Absorber
pv
$\dot{W}$

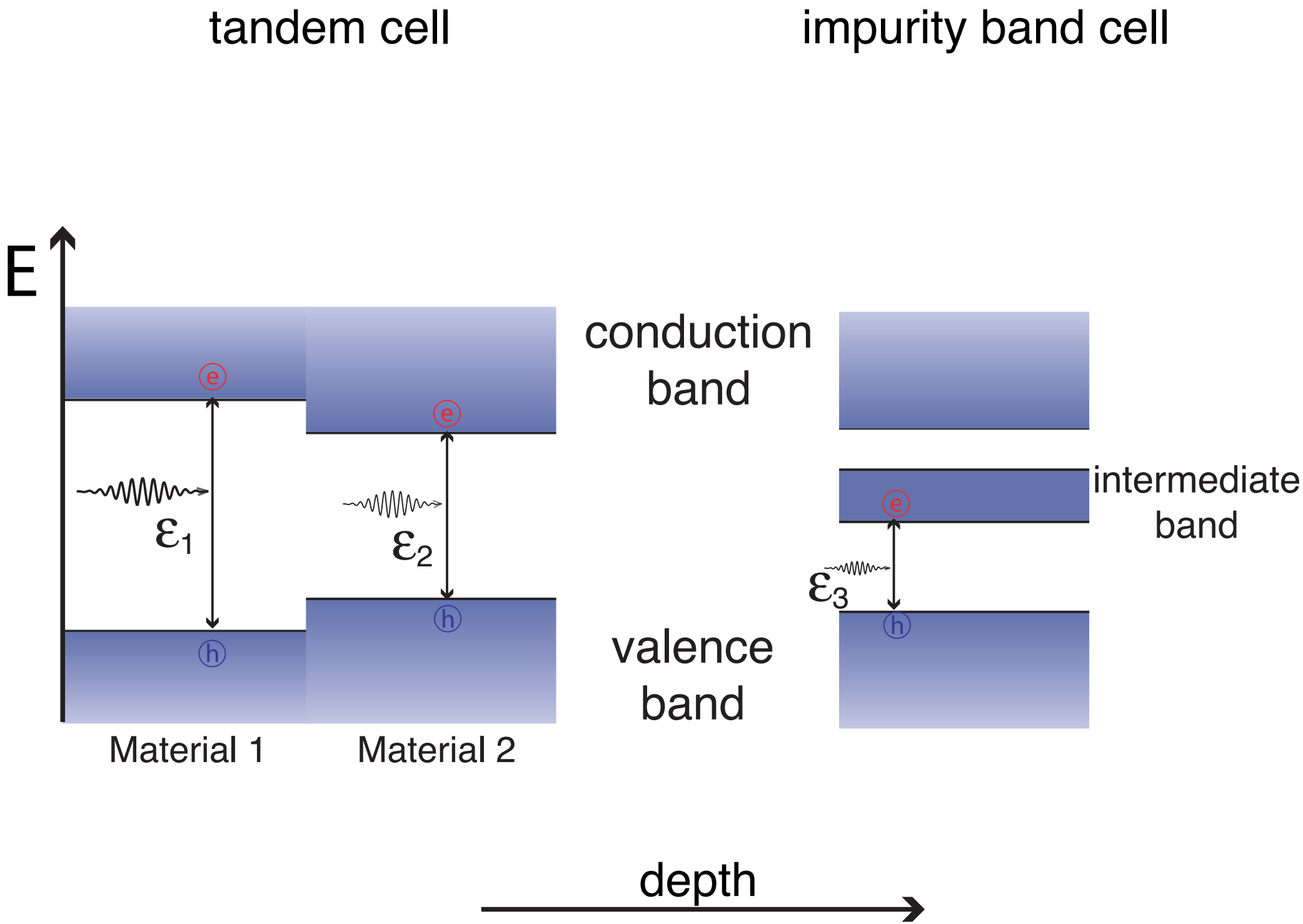
tandem cell

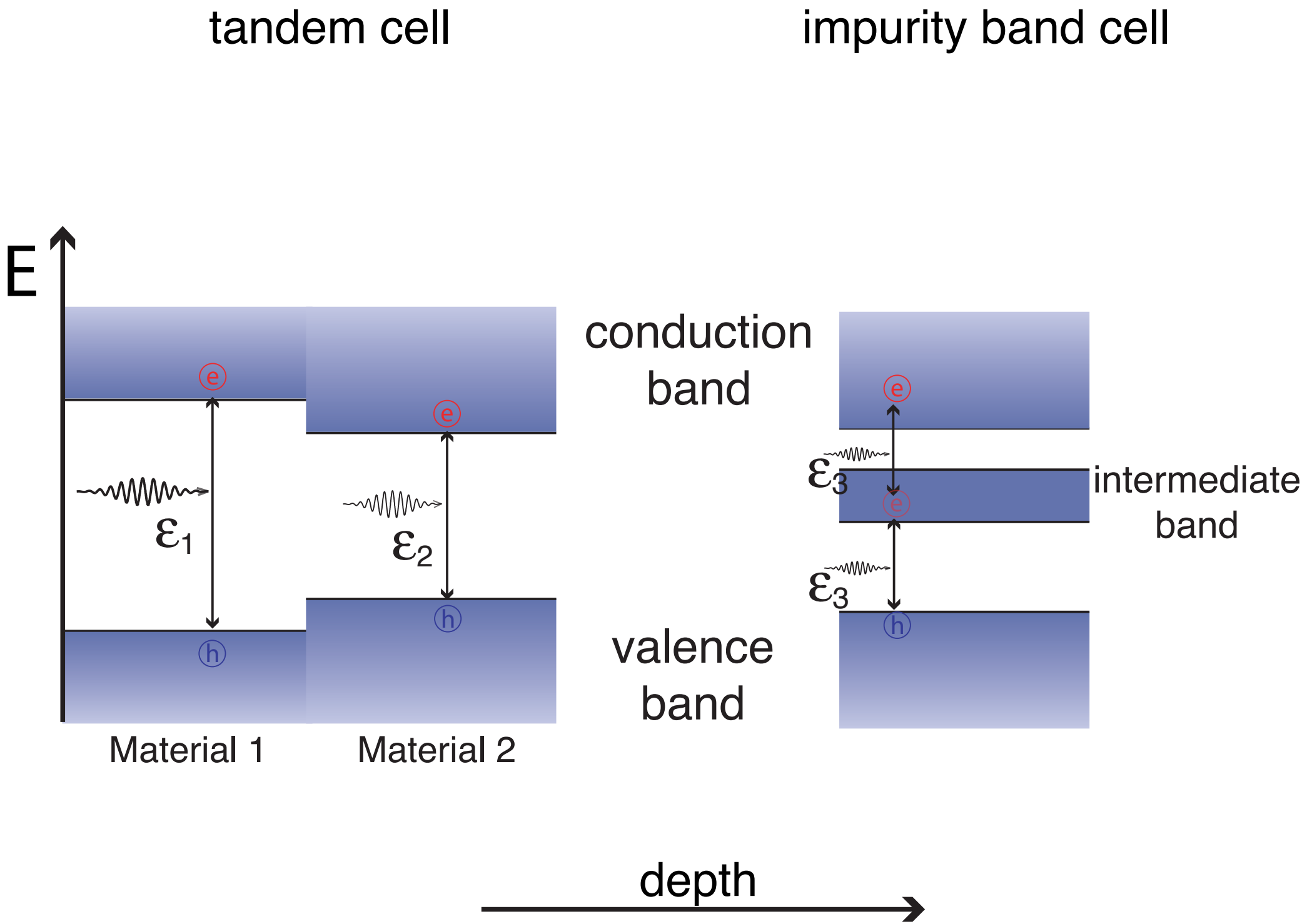


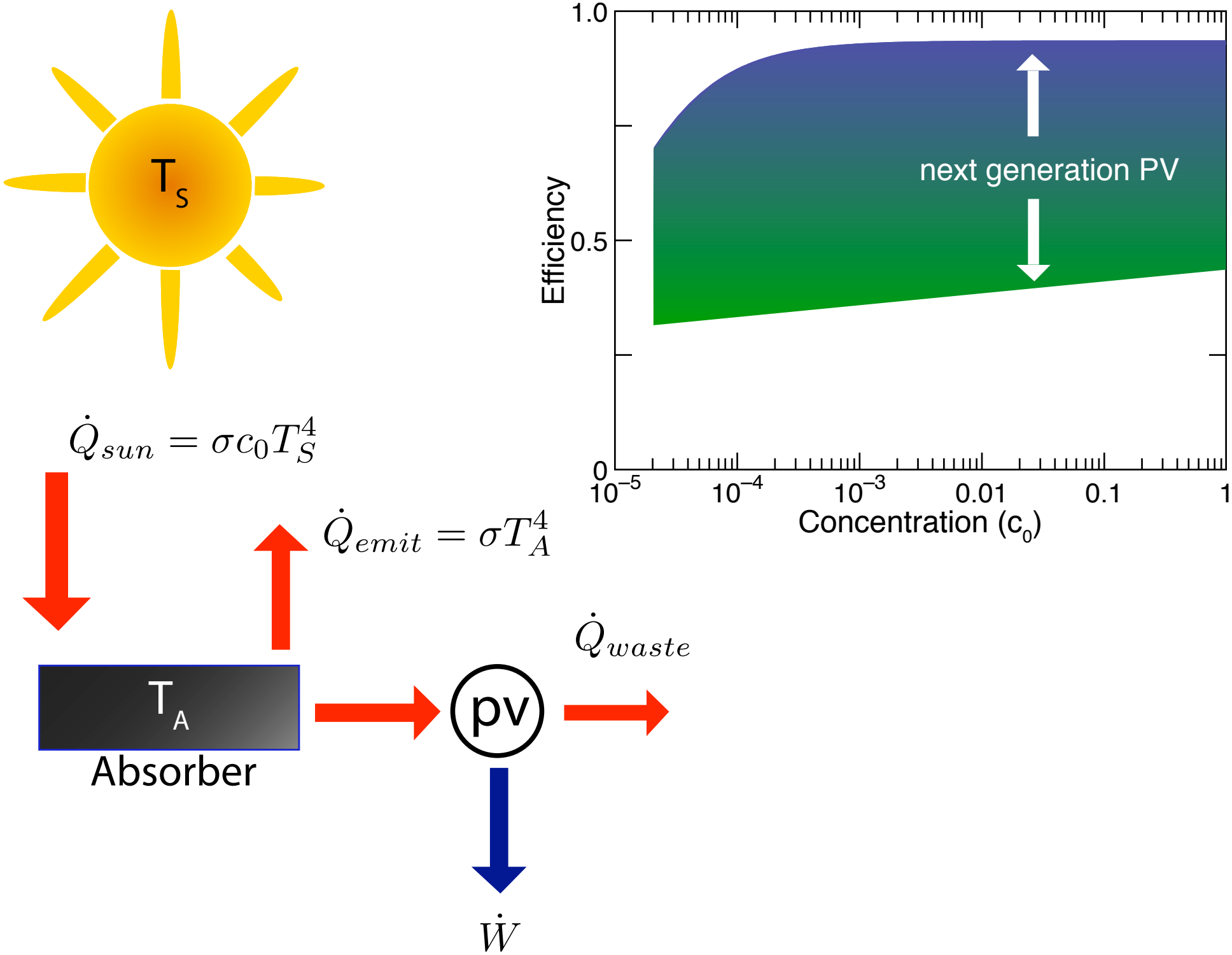
tandem cell

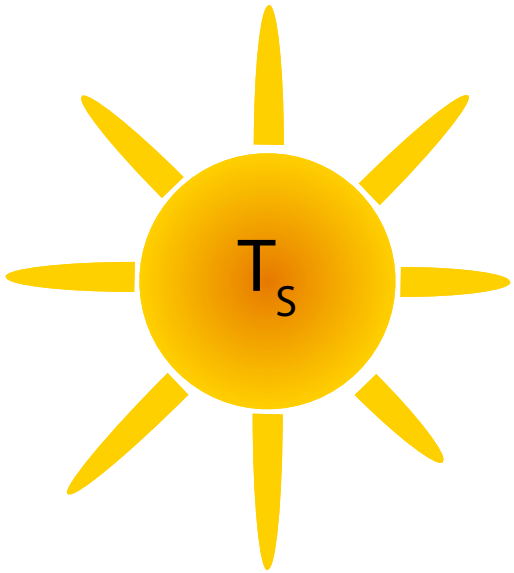

E
e
e
ε_1
ε_2
h
h
conduction band
valence band
Material 1
Material 2
depth

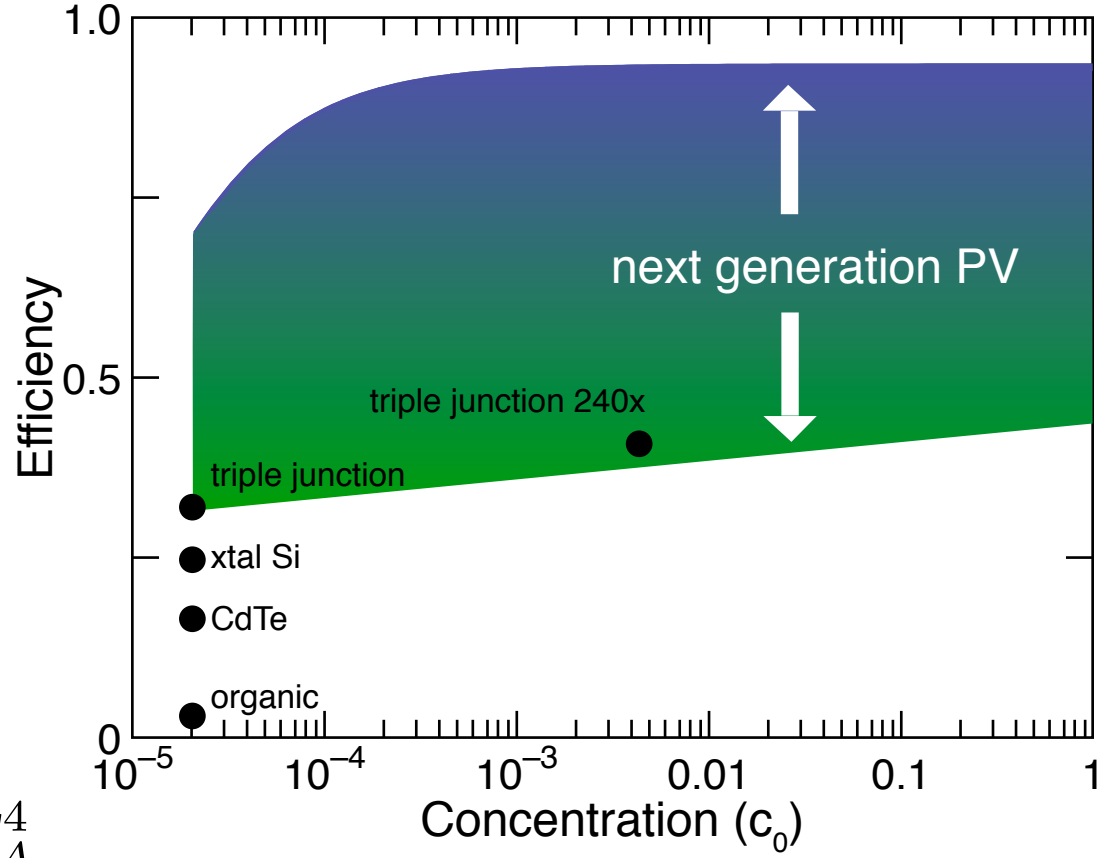

tandem cell
impurity band cell
E
e
e
h
h
ε_1
ε_2
conduction band
valence band
intermediate band
Material 1
Material 2
depth


tandem cell
impurity band cell
E
e
h
ε_1
ε_2
ε_3
conduction band
valence band
intermediate band
Material 1
Material 2
depth


tandem cell
impurity band cell
E
e
h
ε_1
ε_2
Material 1
Material 2
conduction band
valence band
ε_3
intermediate band
depth


T_S
$\dot{Q}_{sun} = \sigma c_0 T_S^4$
$\dot{Q}_{emit} = \sigma T_A^4$
T_A
Absorber
pv
$\dot{Q}_{waste}$
$\dot{W}$
1.0
0.5
0
Efficiency
next generation PV
10^{-5}
10^{-4}
10^{-3}
0.01
0.1
1
Concentration (c_0)

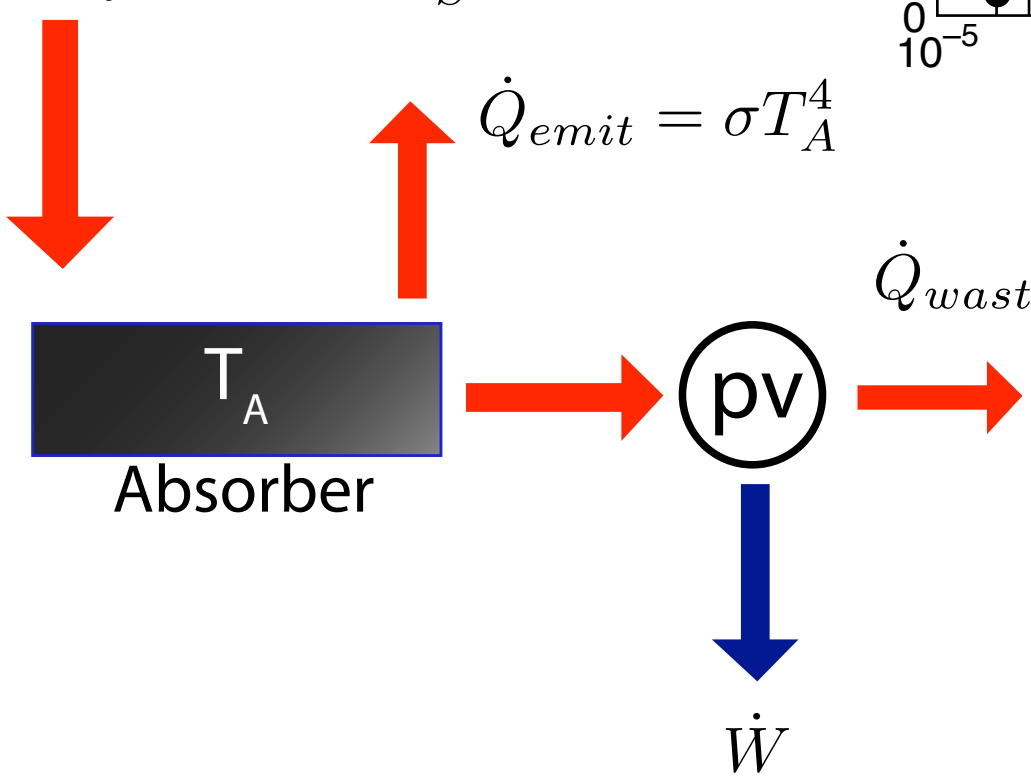




$$\dot{Q}_{sun} = \sigma c_0 T_S^4$$

$$\dot{Q}_{emit} = \sigma T_A^4$$

$$\dot{Q}_{waste}$$



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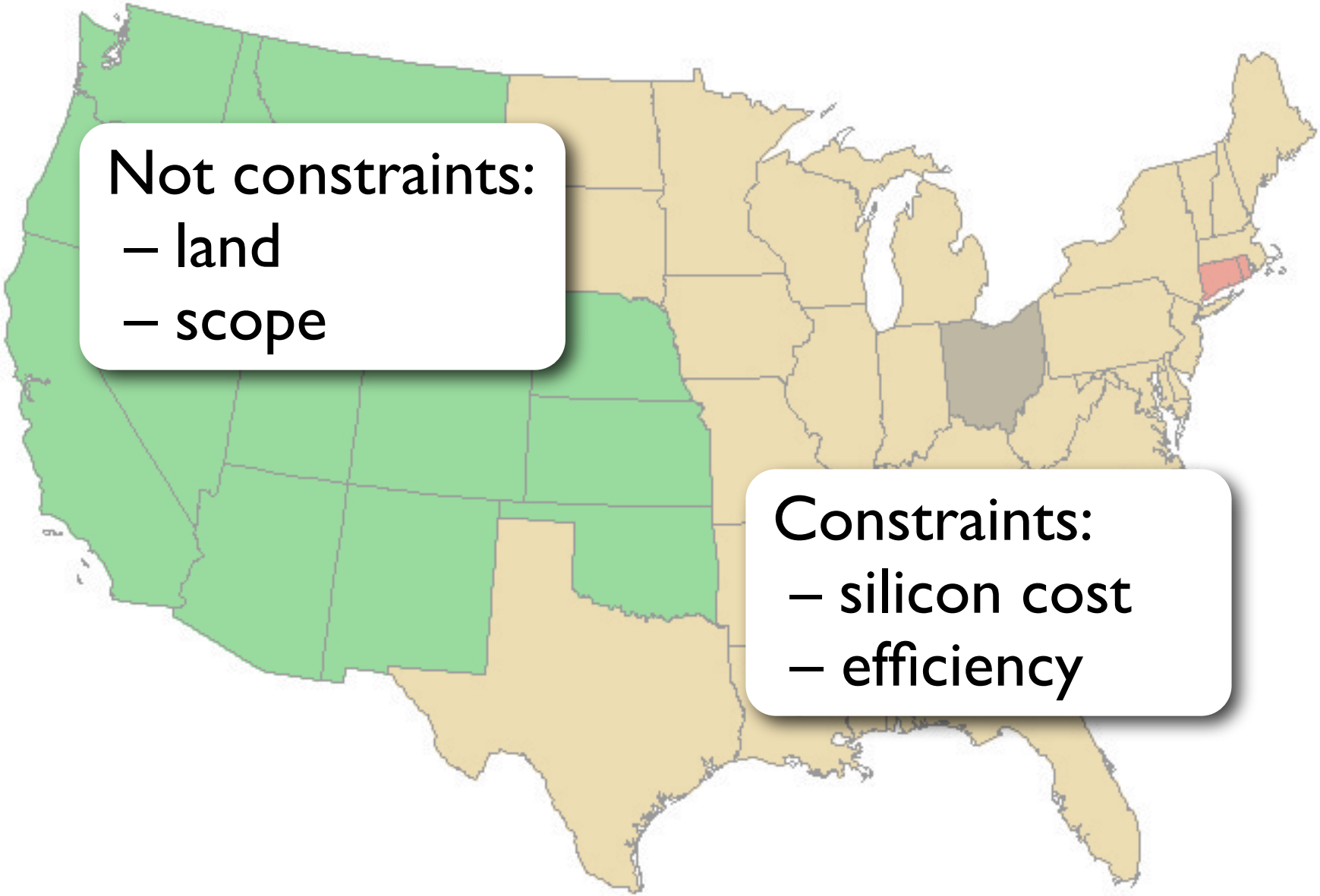
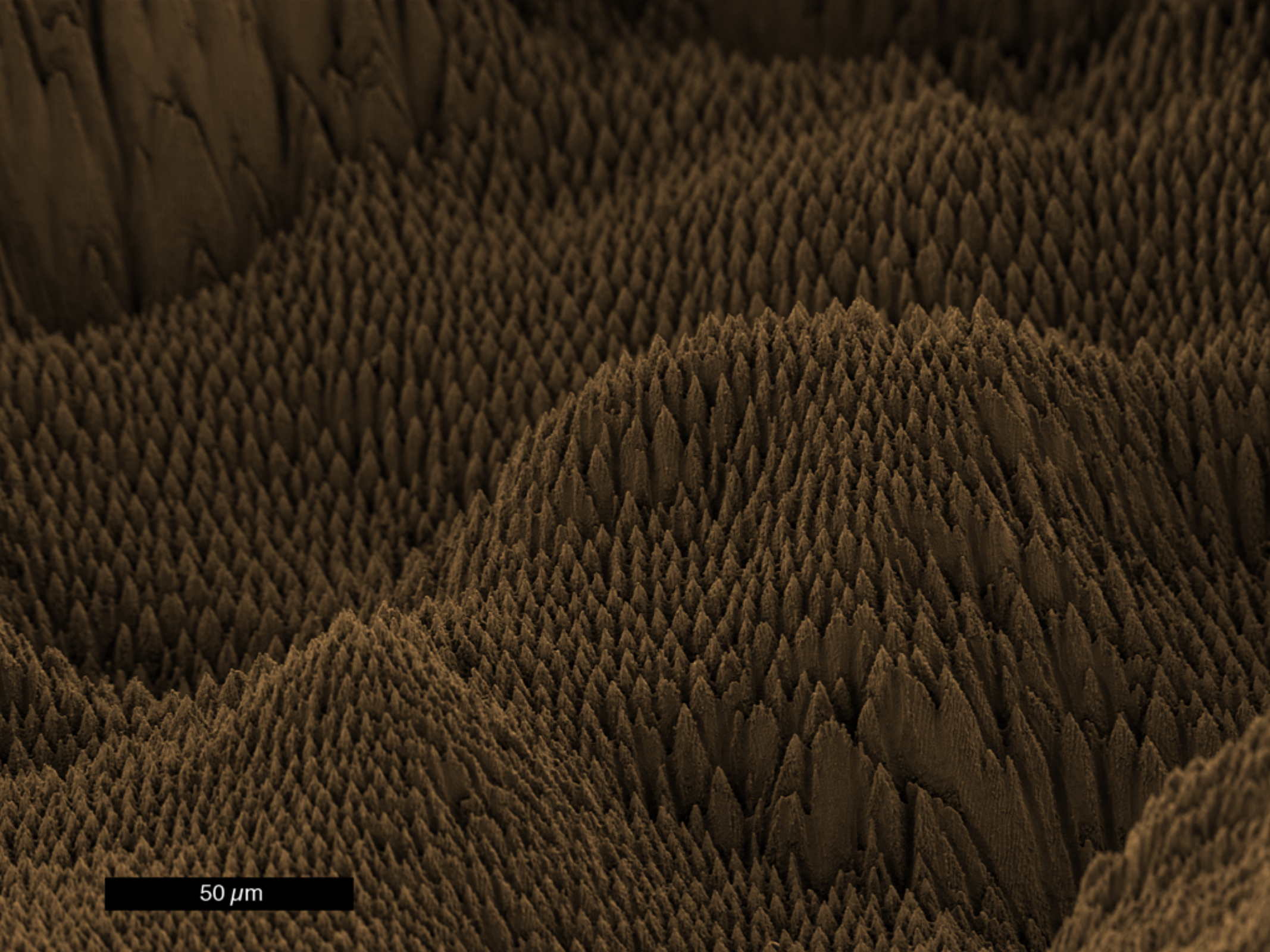
Why extend silicon's reach?




100 μm


50 μm

Understanding a material that extends silicon's reach:

Understanding a material that extends silicon's reach:

- What we know about laser doping of silicon

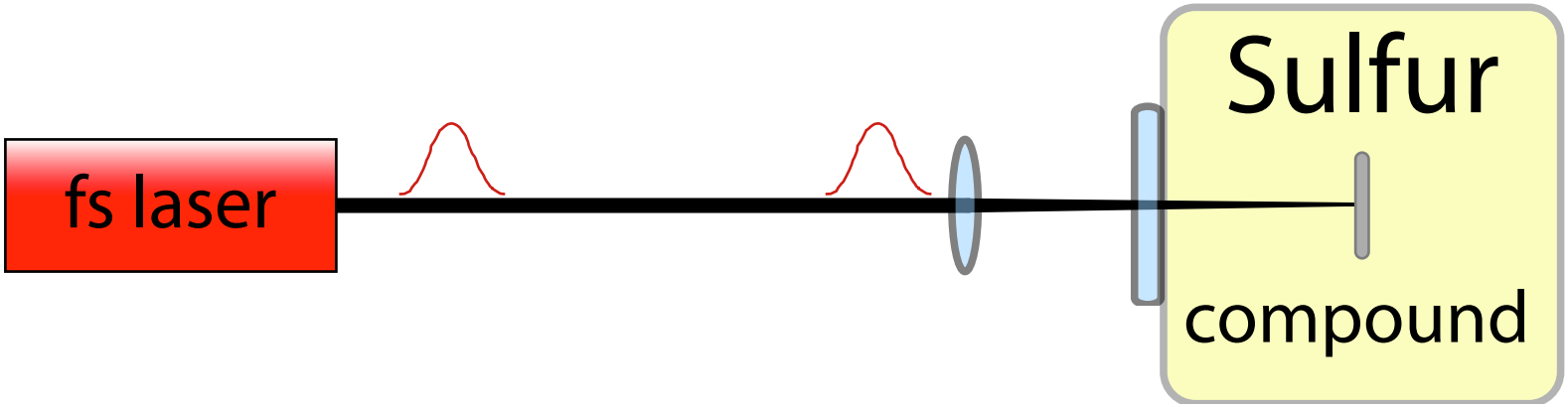
Understanding a material that extends silicon's reach:

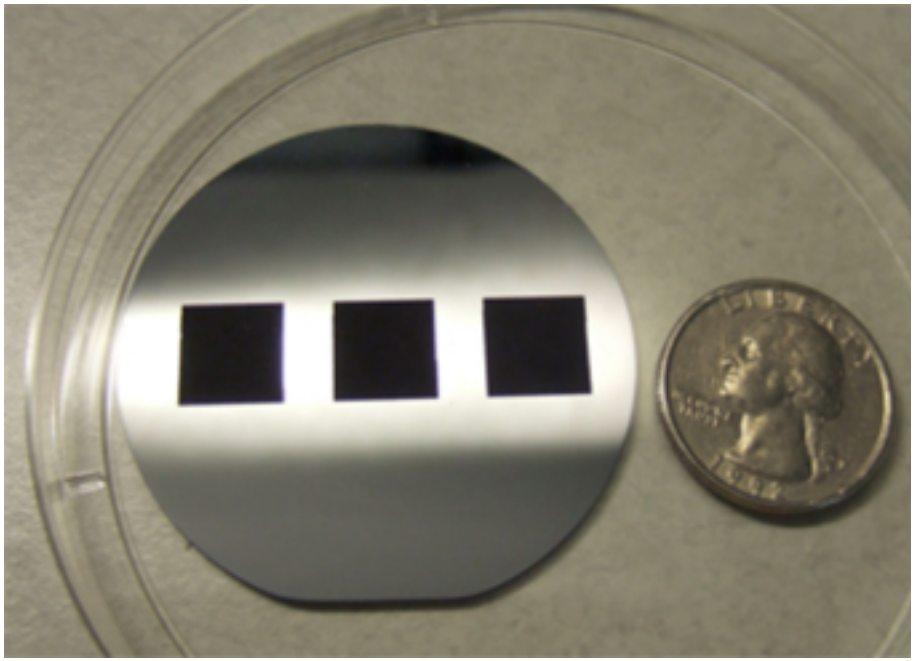
- What we know about laser doping of silicon
- Structural role of dopants in infrared absorptance

Understanding a material that extends silicon's reach:

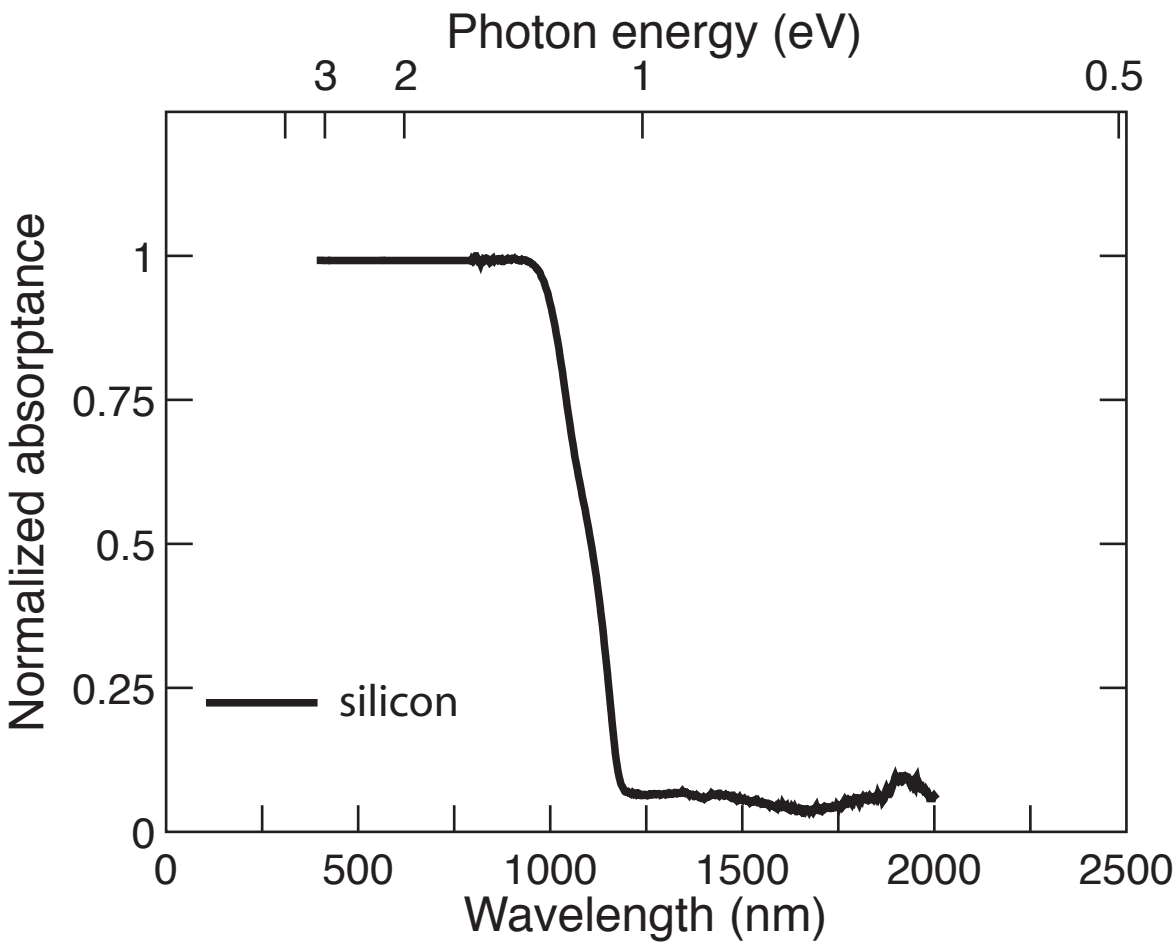
- What we know about laser doping of silicon
- Structural role of dopants in infrared absorptance
- New developments and directions

femtosecond laser doped silicon

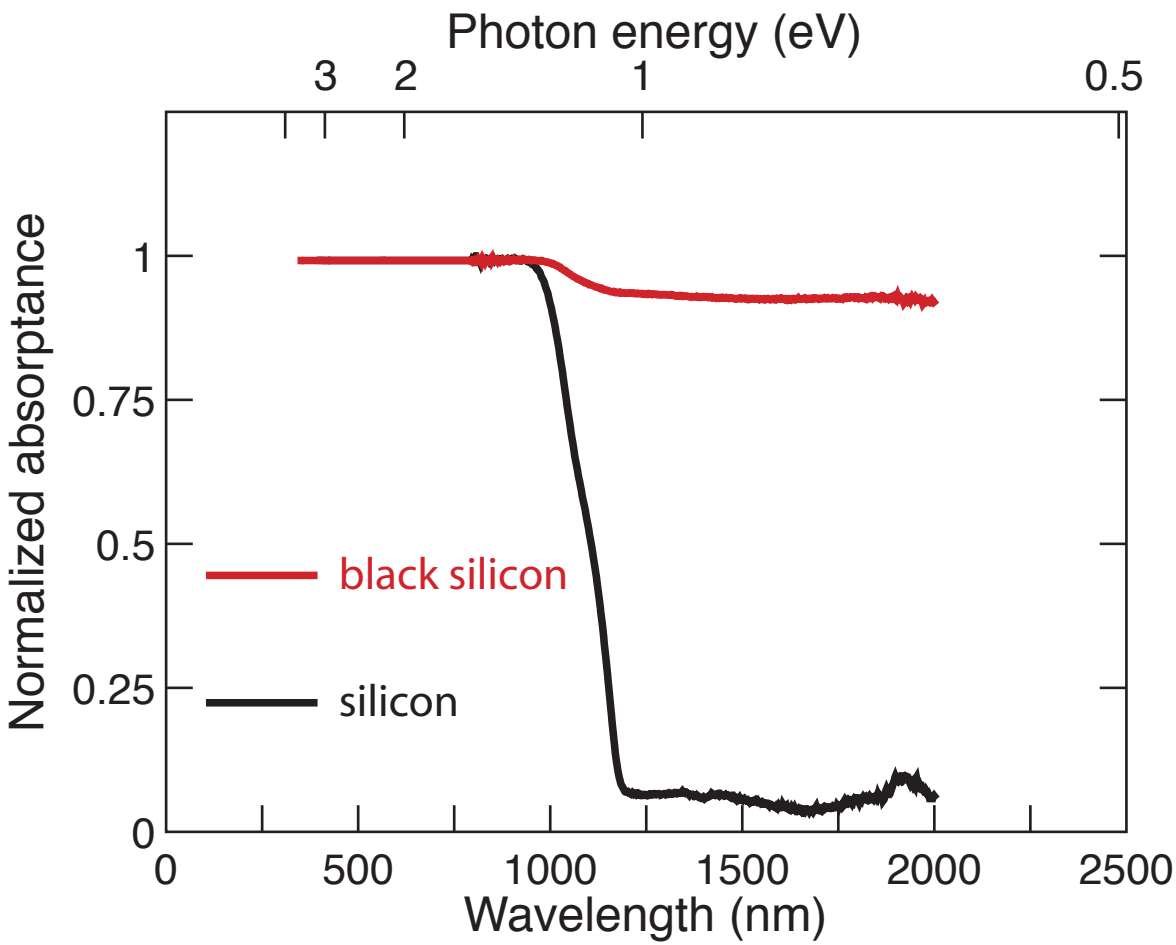




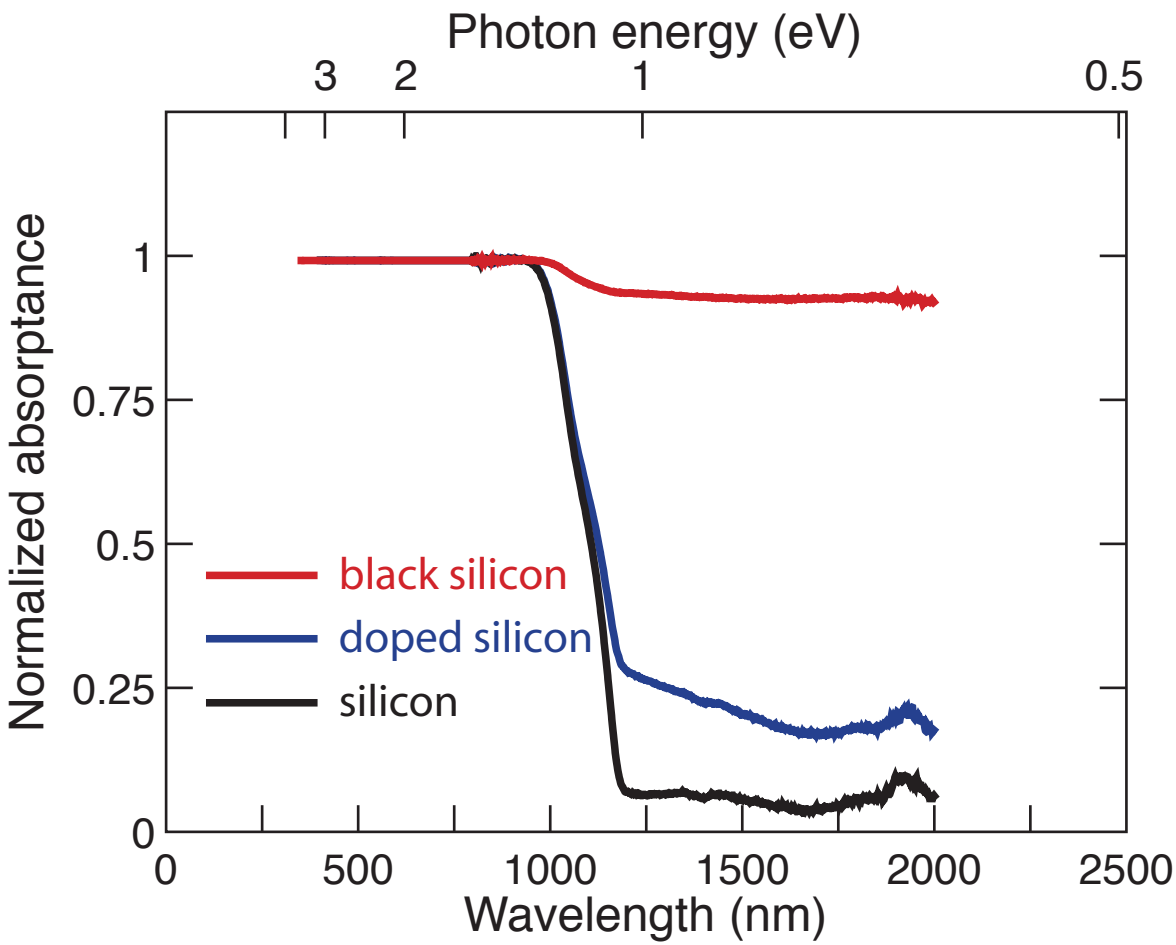
$$\overline{A} = \frac{1-R-T}{1-R}$$

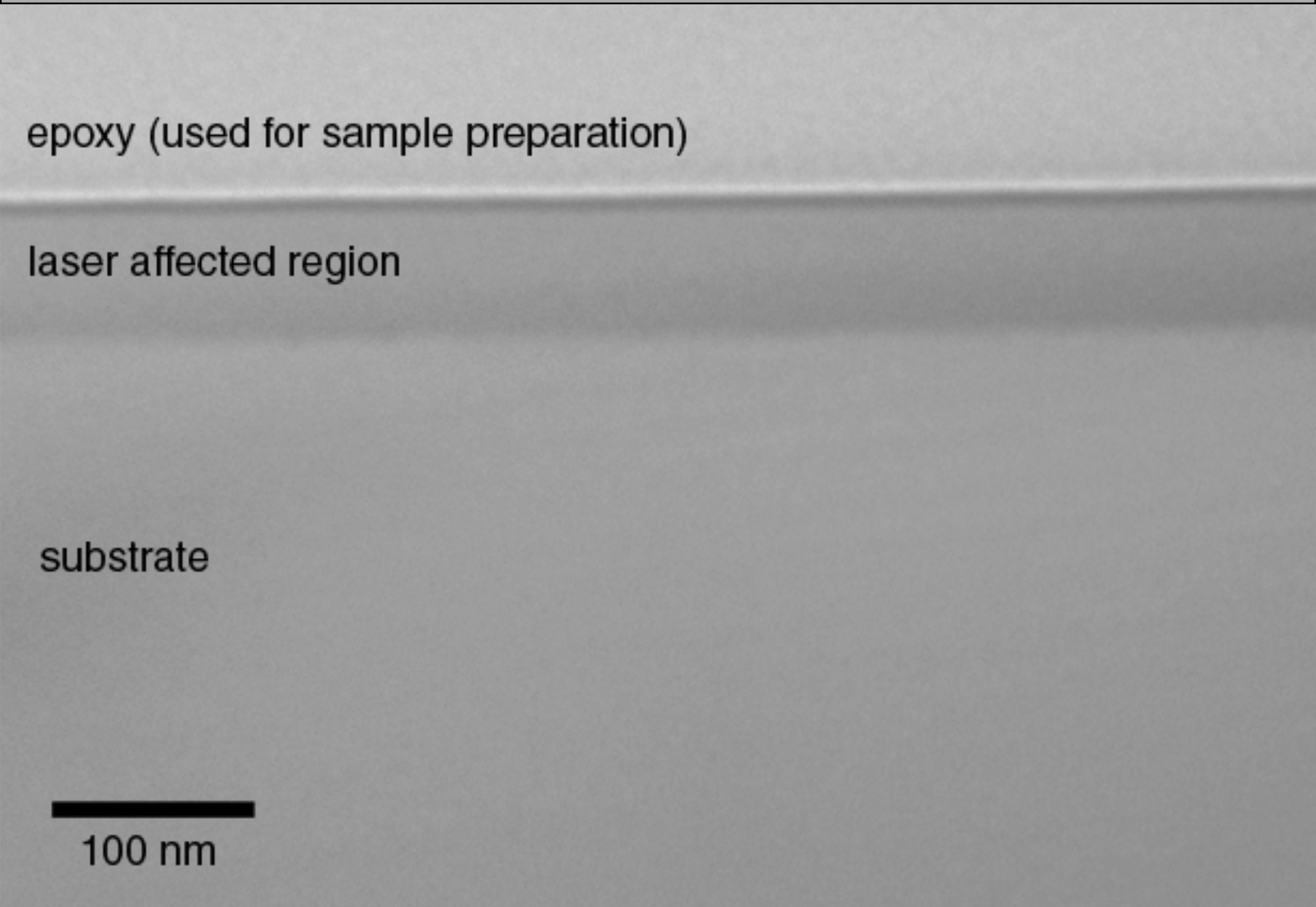


$$\overline{A} = \frac{1-R-T}{1-R}$$



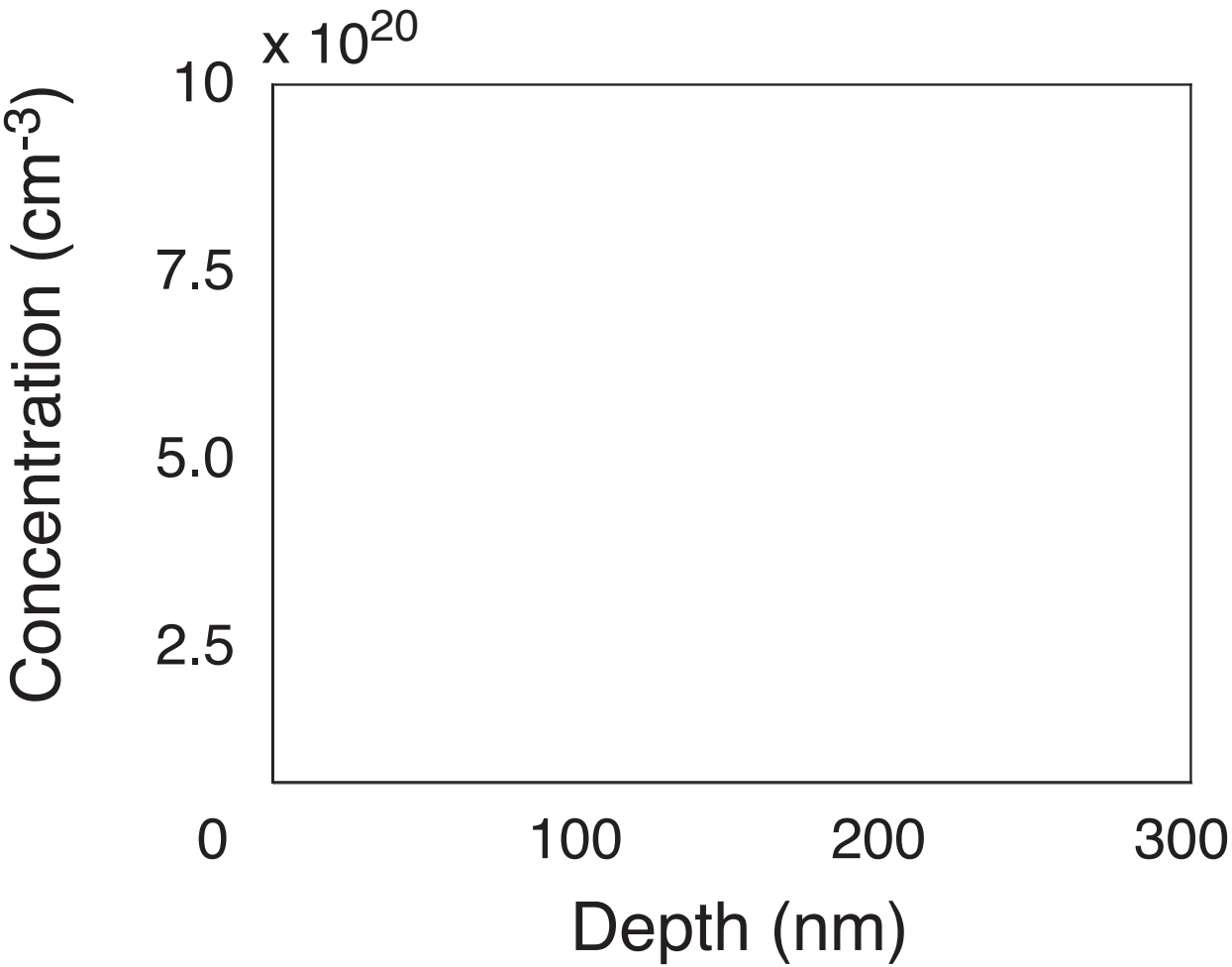
$$\overline{A} = \frac{1-R-T}{1-R}$$




epoxy (used for sample preparation)
laser affected region
substrate
100 nm

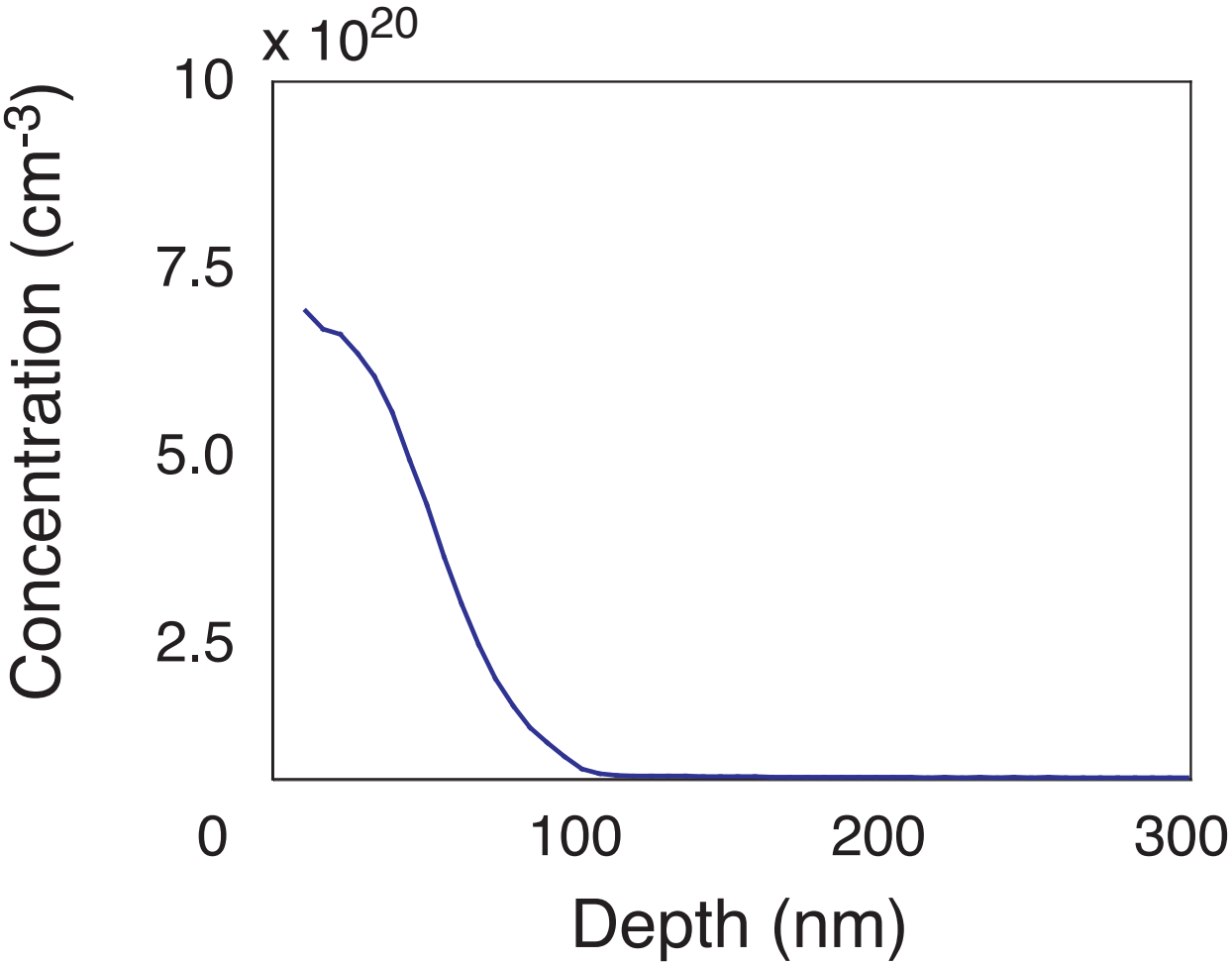
fs lasers dope beyond equilibrium limit

secondary ion mass spectroscopy (SIMS)



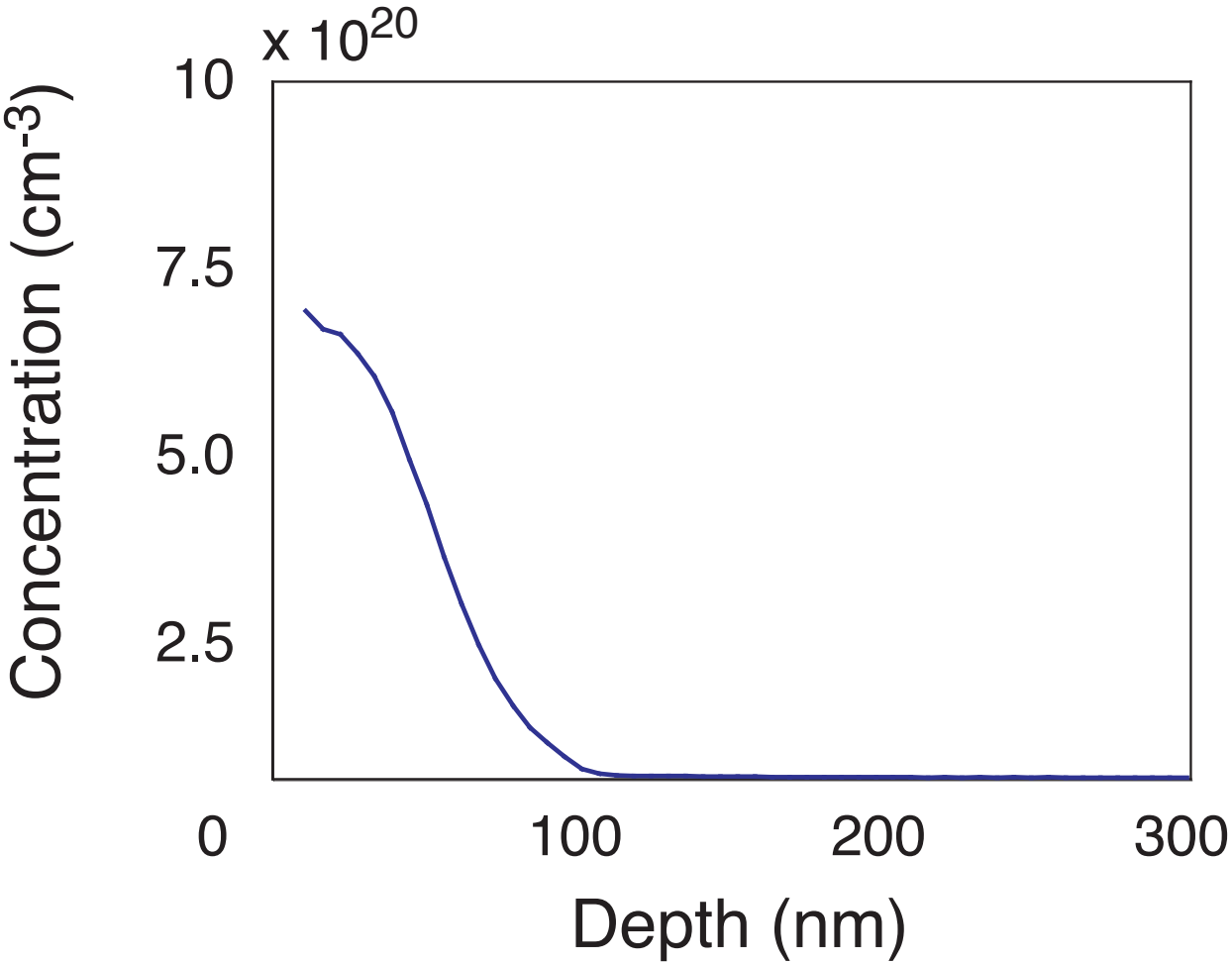
fs lasers dope beyond equilibrium limit

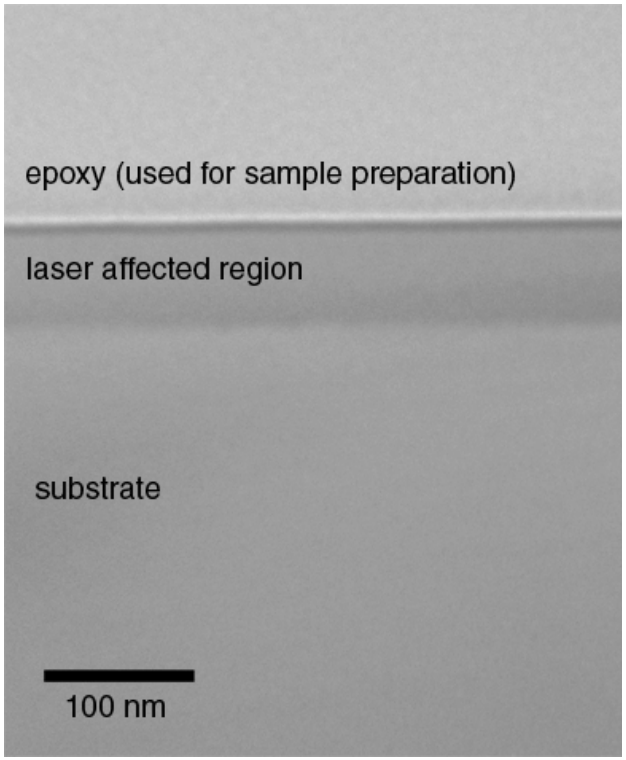
secondary ion mass spectroscopy (SIMS)



fs lasers dope beyond equilibrium limit

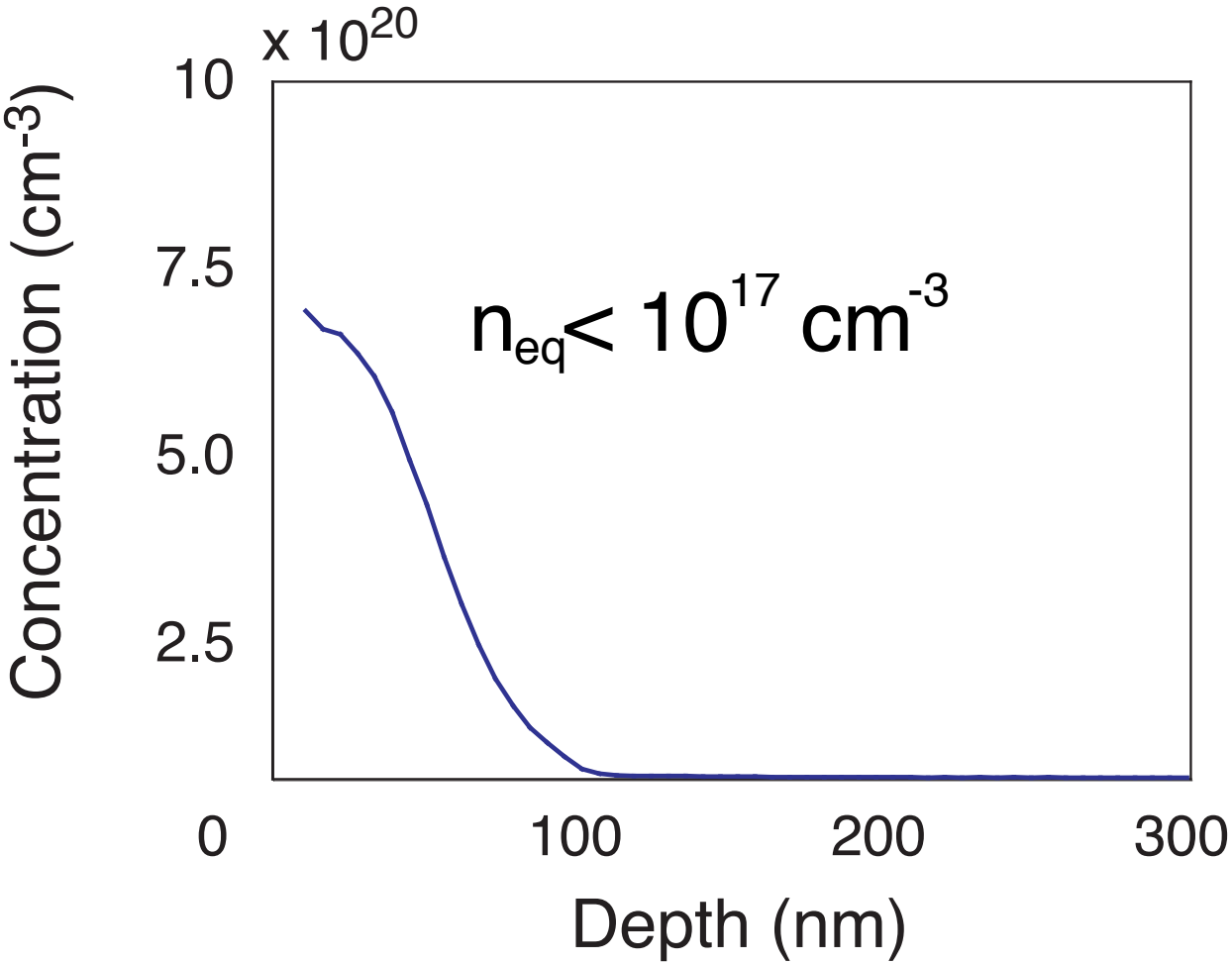
secondary ion mass spectroscopy (SIMS)

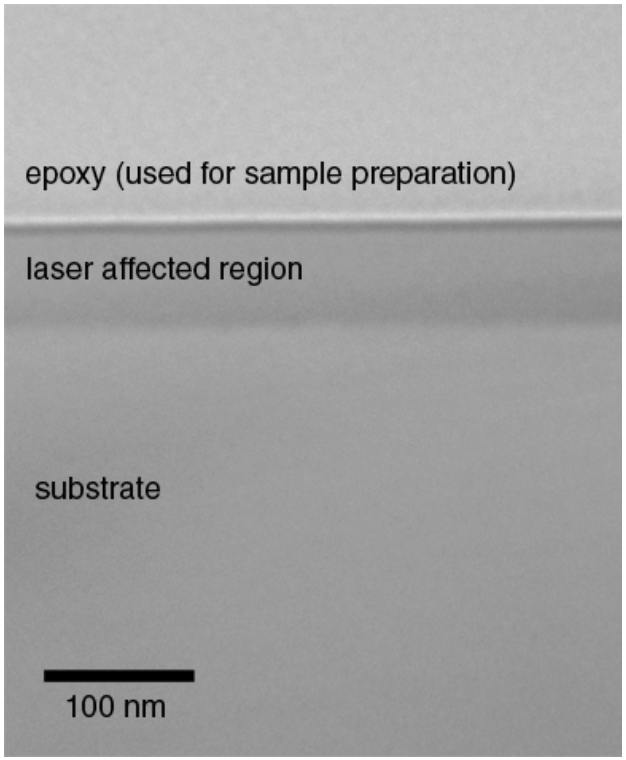


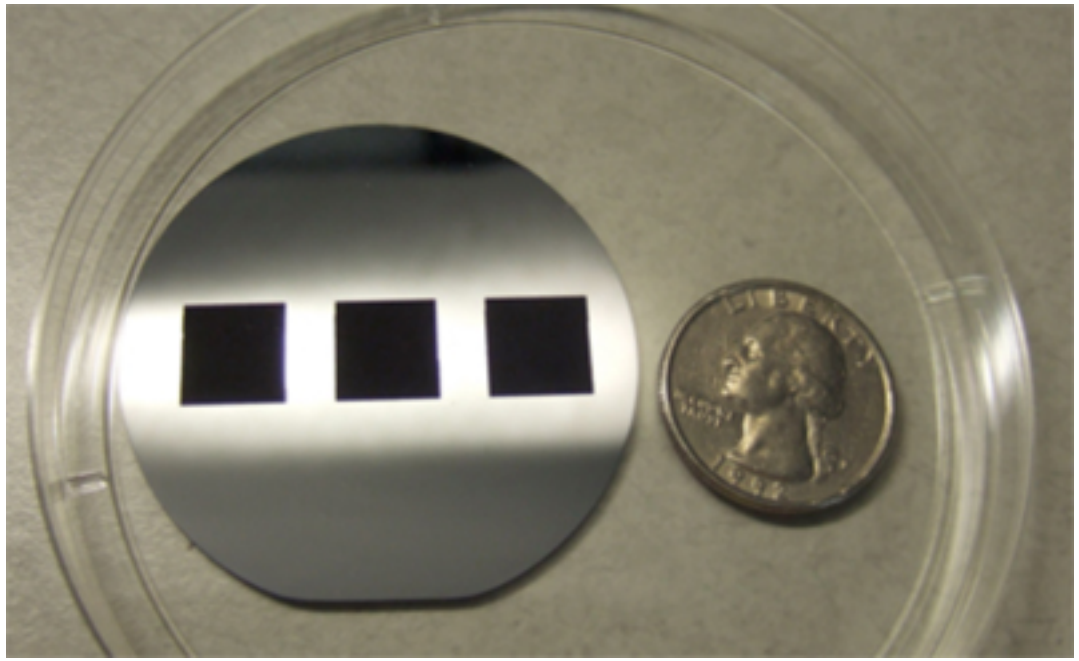


fs lasers dope beyond equilibrium limit

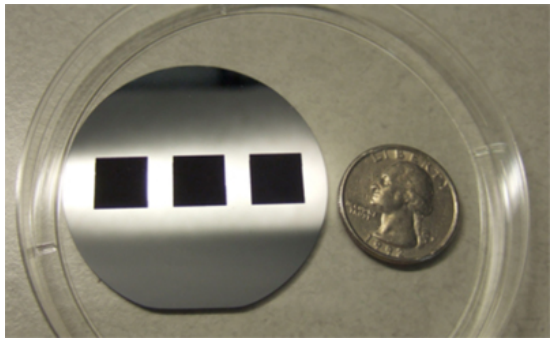
secondary ion mass spectroscopy (SIMS)



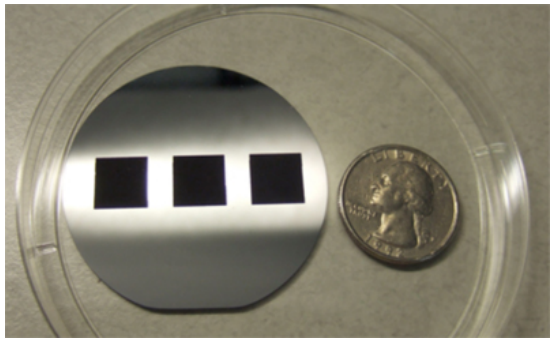


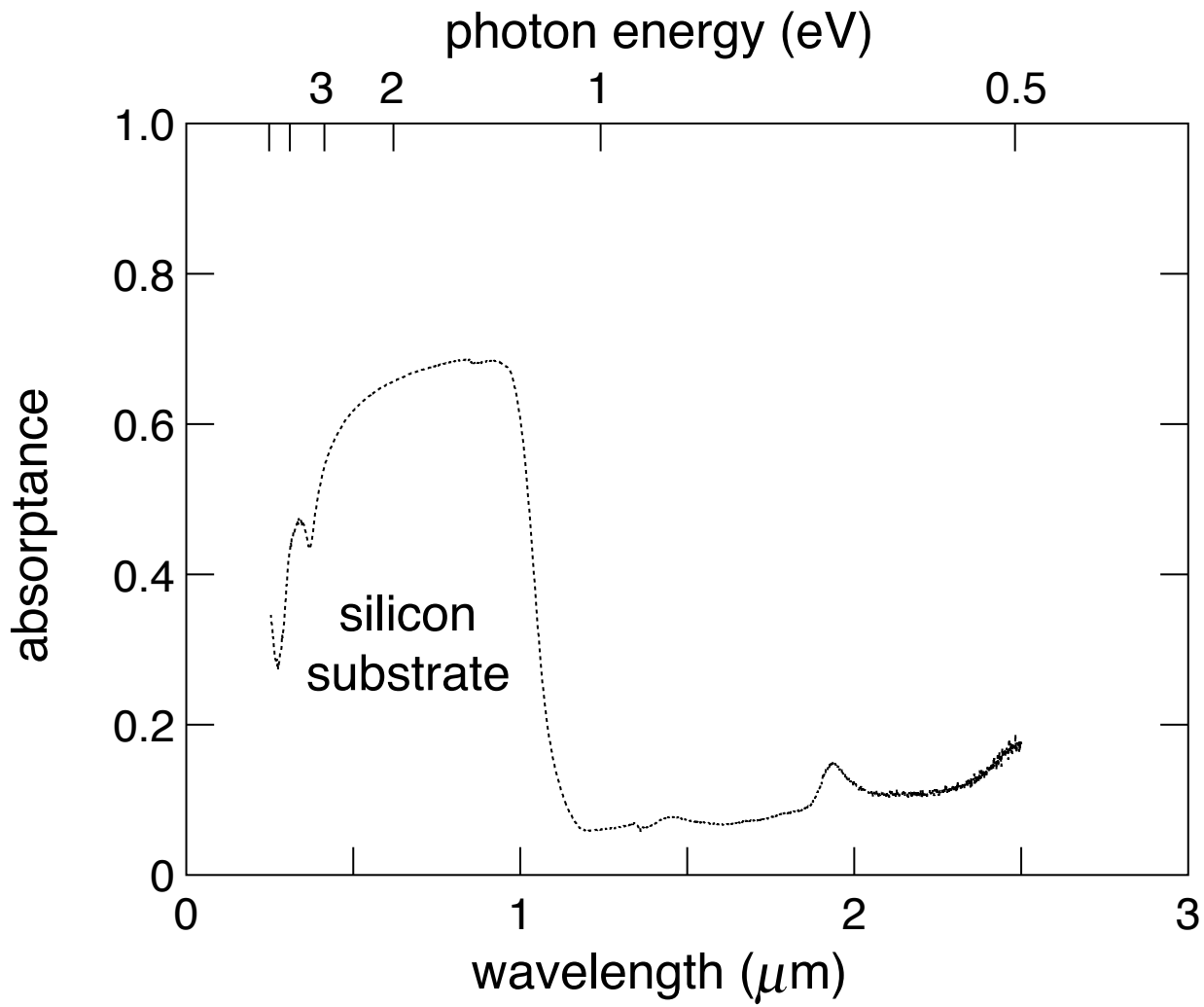


fs laser
Sulfur
compound

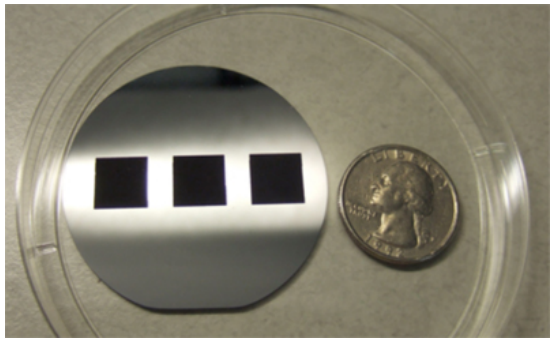


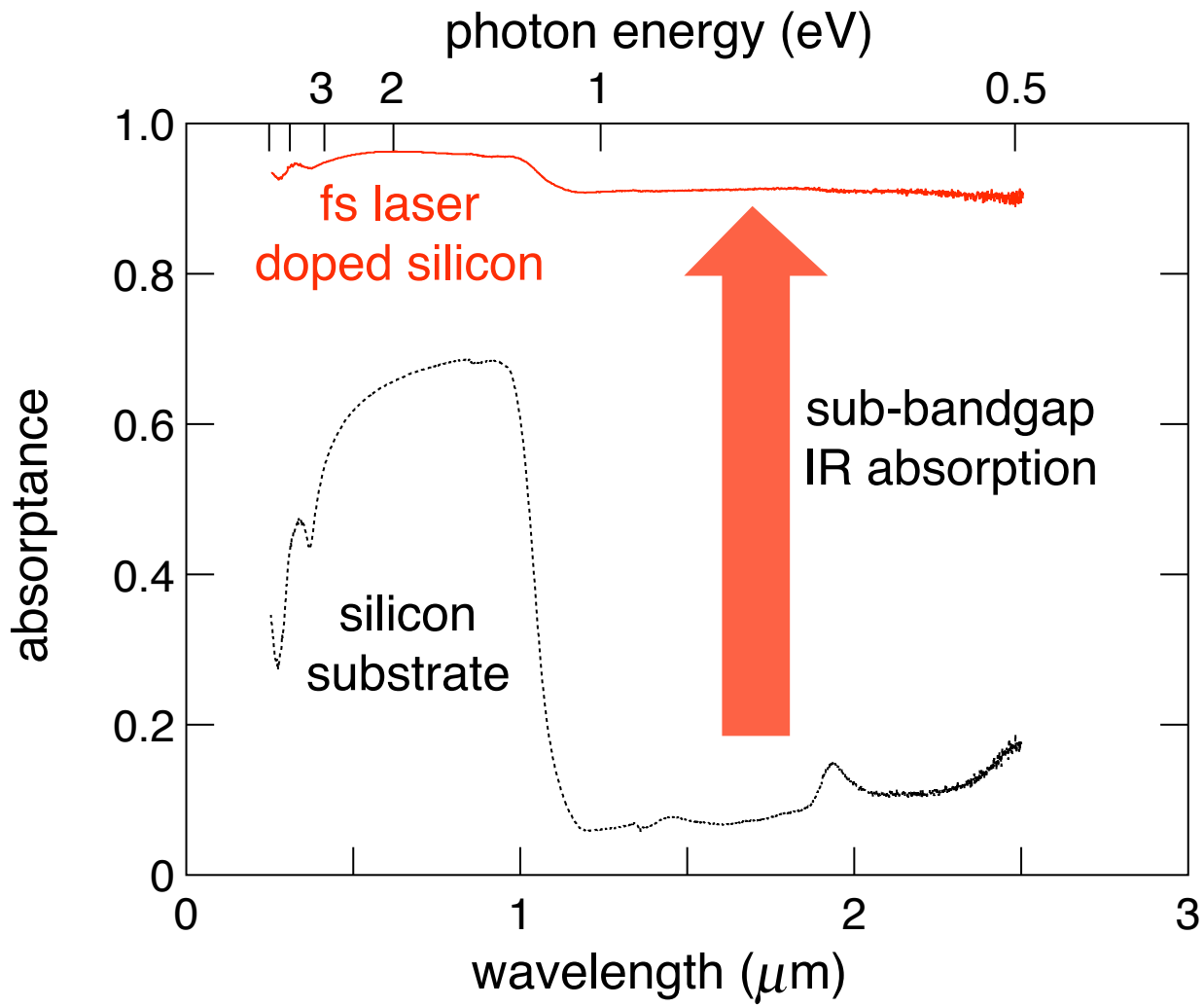
fs laser
Sulfur
compound



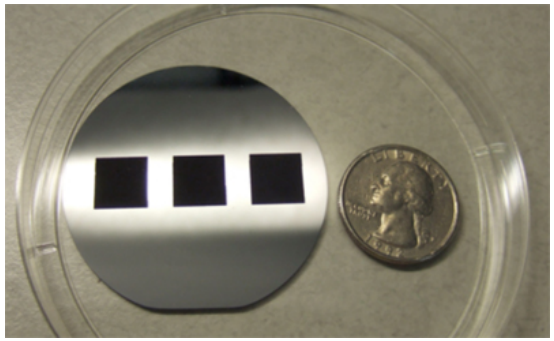

photon energy (eV)
3
2
1
0.5
1.0
0.8
0.6
0.4
0.2
0
absorptance
silicon
substrate
0
1
2
3
wavelength (μm)

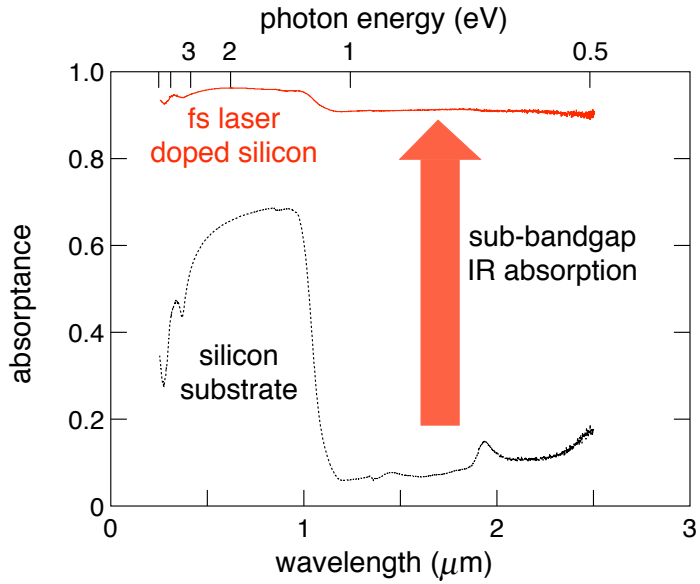
fs laser
Sulfur
compound



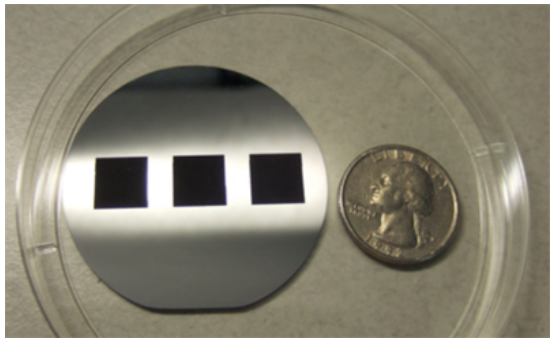

photon energy (eV)
3
2
1
0.5
1.0
0.8
0.6
0.4
0.2
0
absorptance
fs laser
doped silicon
sub-bandgap
IR absorption
silicon
substrate
0
1
2
3
wavelength (μm)

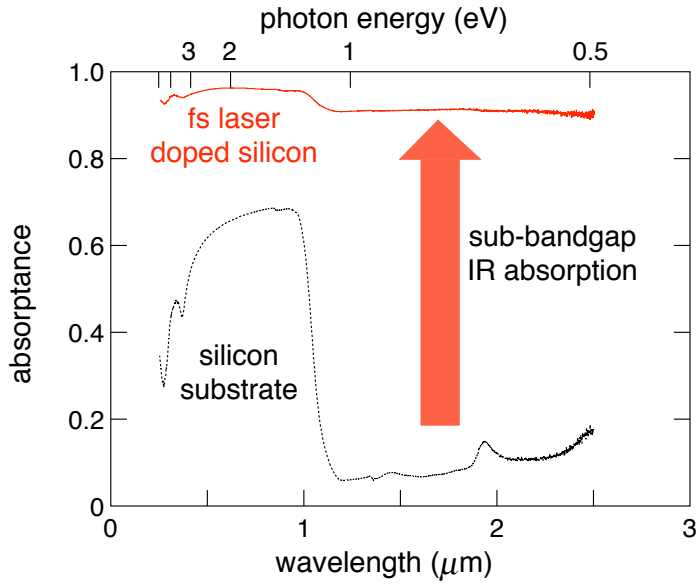
fs laser
Sulfur
compound

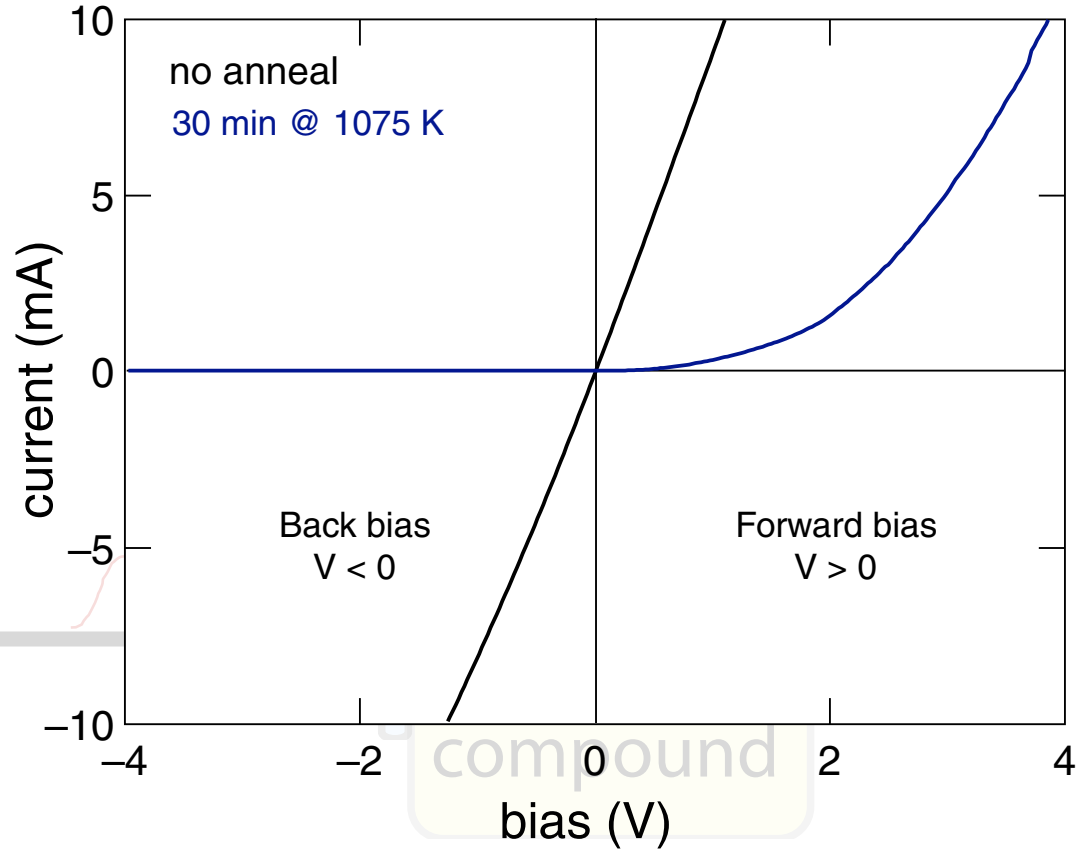



photon energy (eV)
3
2
1
0.5
1.0
0.8
0.6
0.4
0.2
0
absorptance
fs laser
doped silicon
sub-bandgap
IR absorption
silicon
substrate
0
1
2
3
wavelength (μm)

fs laser
Sulfur
compound

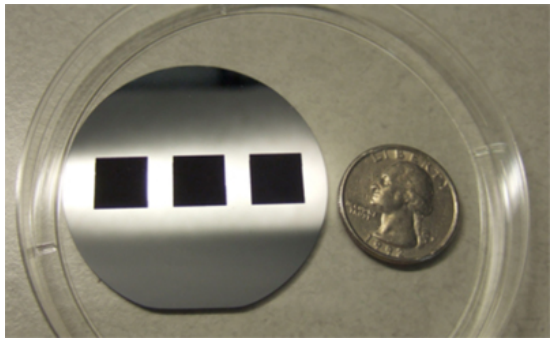


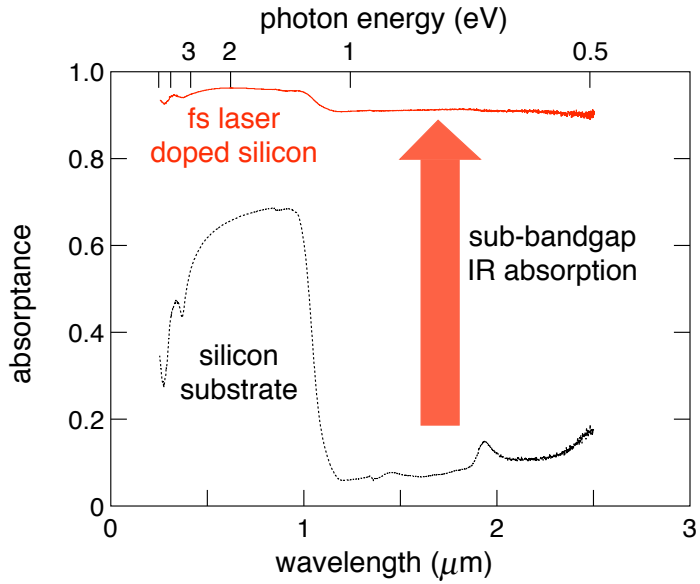


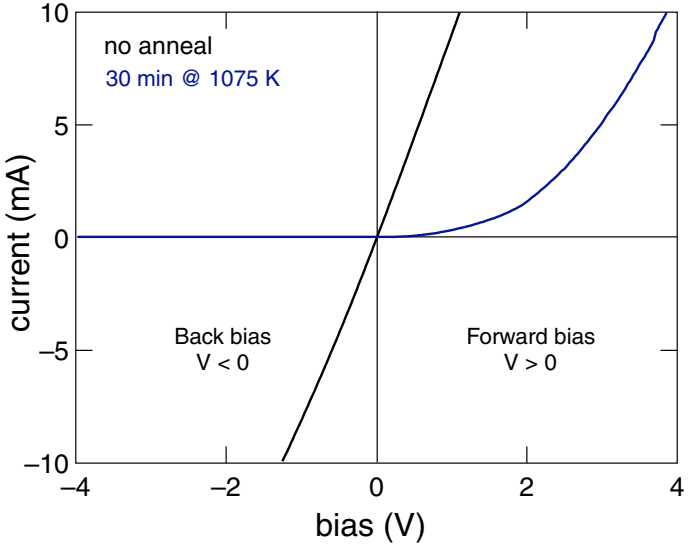


fs laser

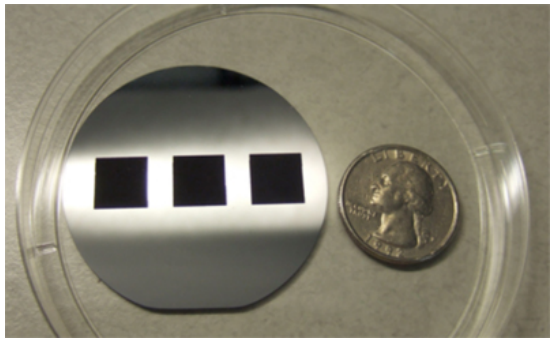
compound

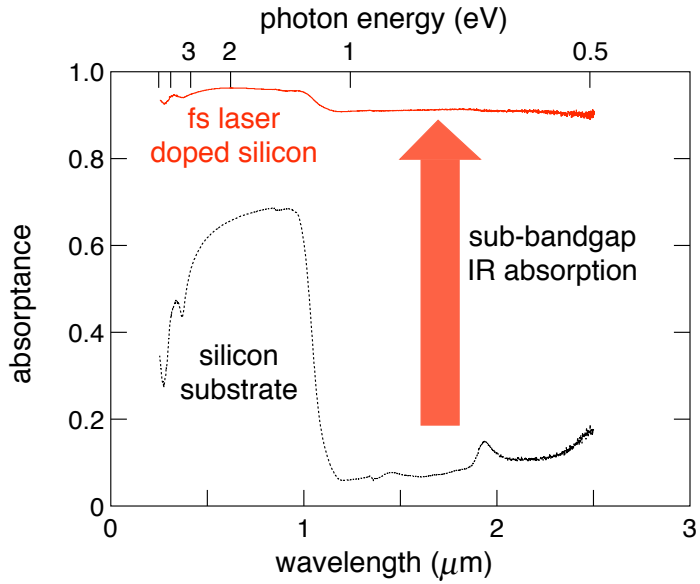


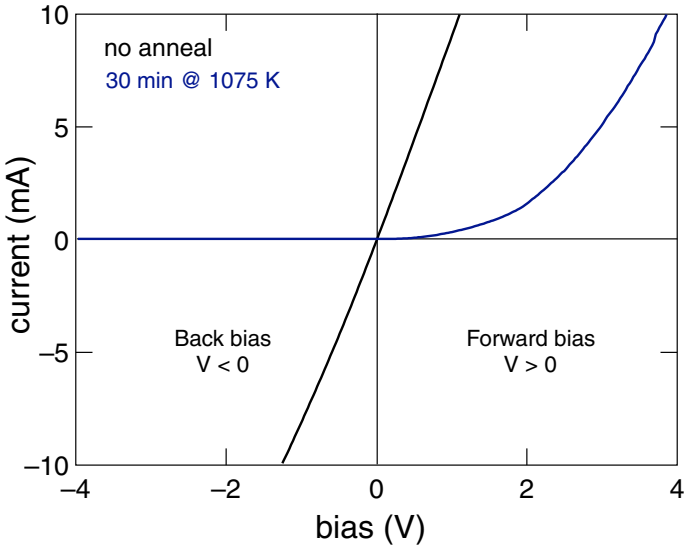

photon energy (eV)
3
2
1
0.5
1.0
0.8
0.6
0.4
0.2
0
absorptance
fs laser
doped silicon
sub-bandgap
IR absorption
silicon
substrate
0
1
2
3
wavelength (μm)


10
5
0
−5
−10
current (mA)
no anneal
30 min @ 1075 K
Back bias
V < 0
Forward bias
V > 0
−4
−2
0
2
4
bias (V)

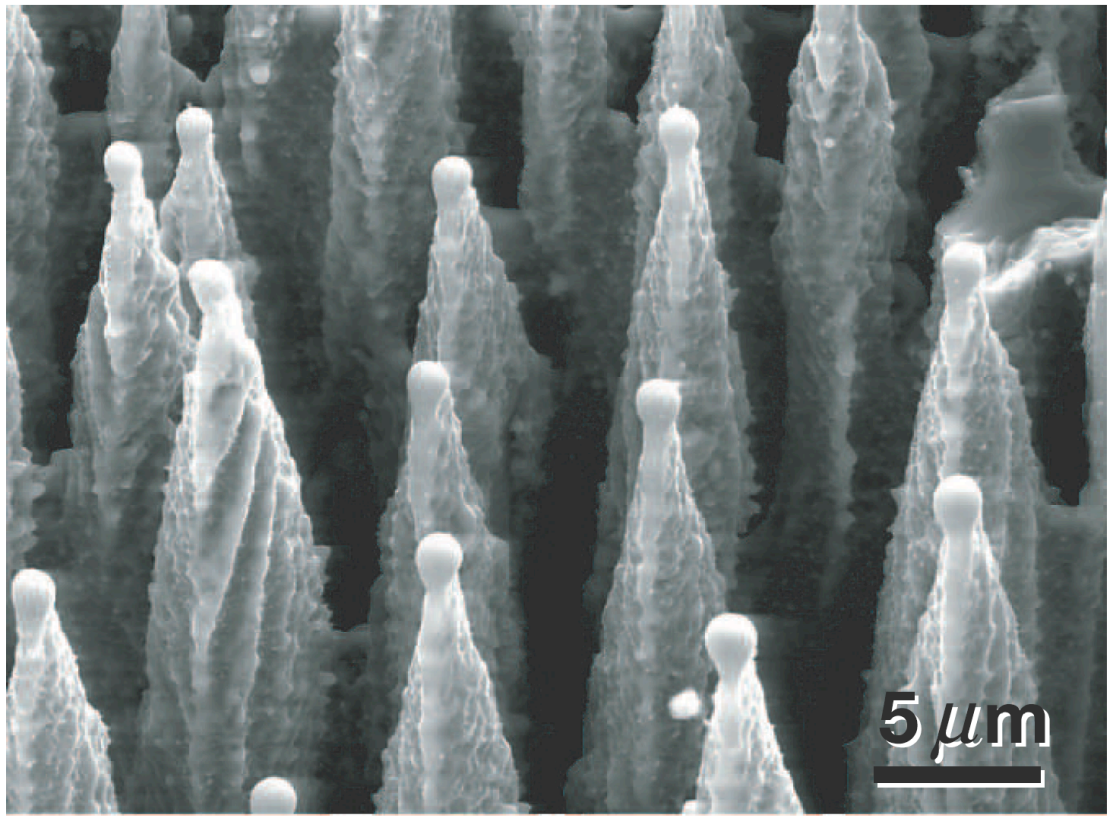
fs laser
Sulfur
compound

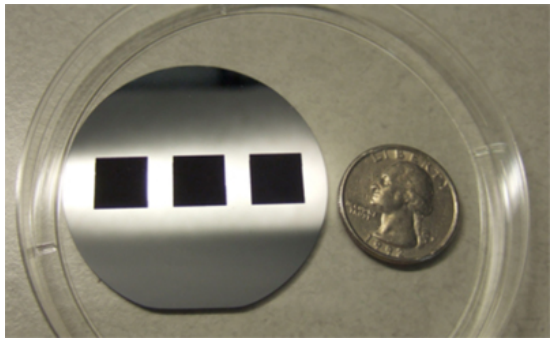


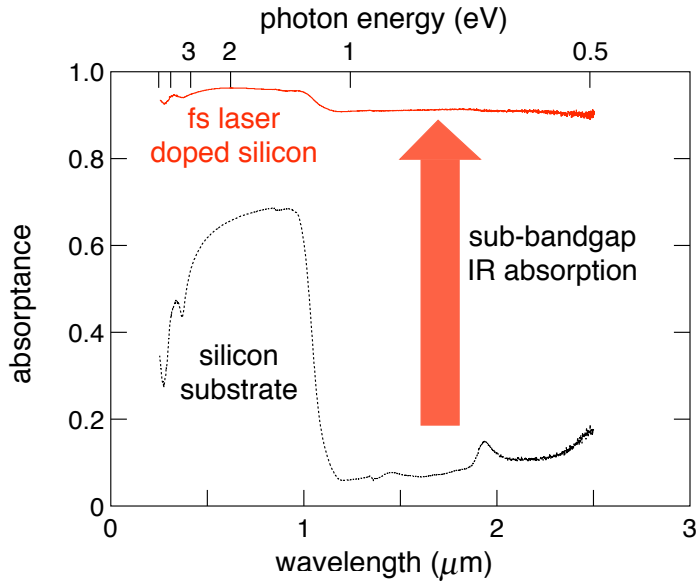

photon energy (eV)
3
2
1
0.5
1.0
0.8
0.6
0.4
0.2
0
absorptance
fs laser
doped silicon
sub-bandgap
IR absorption
silicon
substrate
0
1
2
3
wavelength (μm)

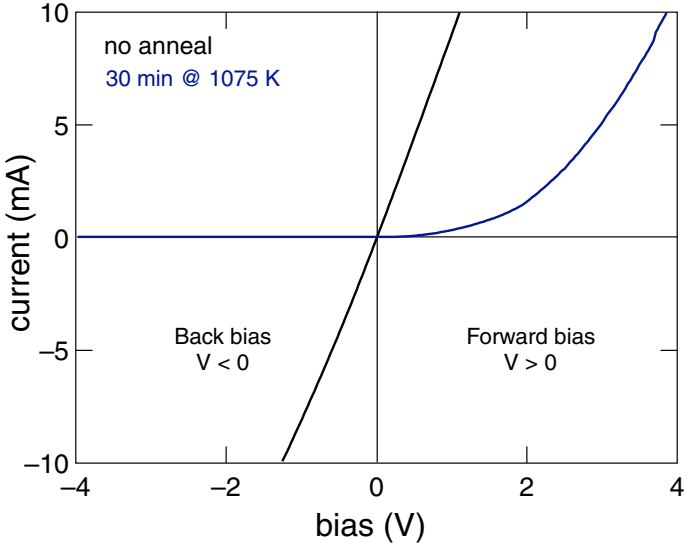

10
5
0
−5
−10
current (mA)
no anneal
30 min @ 1075 K
Back bias
V < 0
Forward bias
V > 0
−4
−2
0
2
4
bias (V)

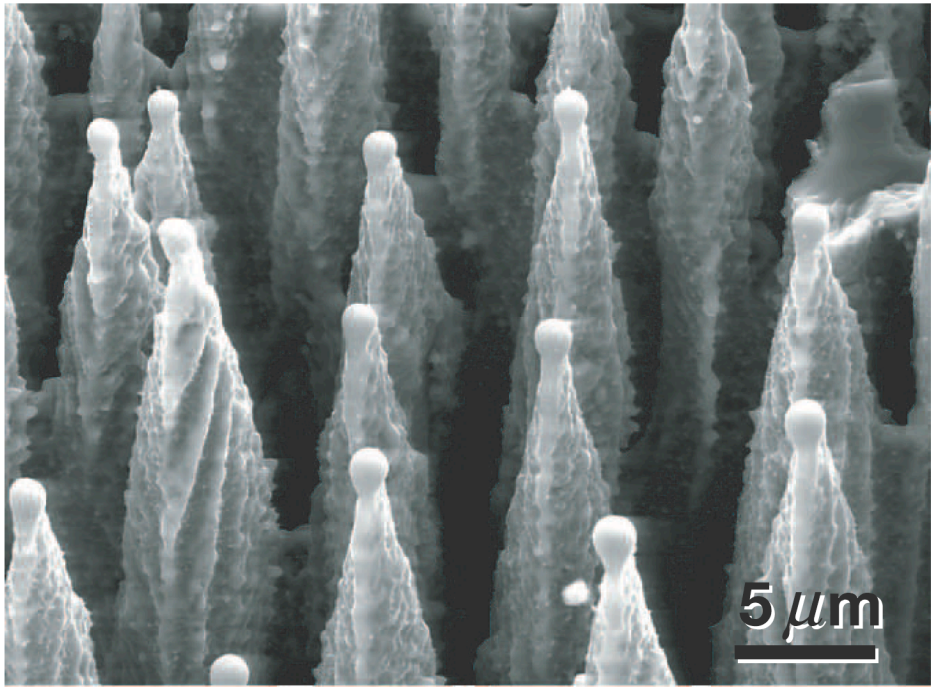
fs laser


5 μm

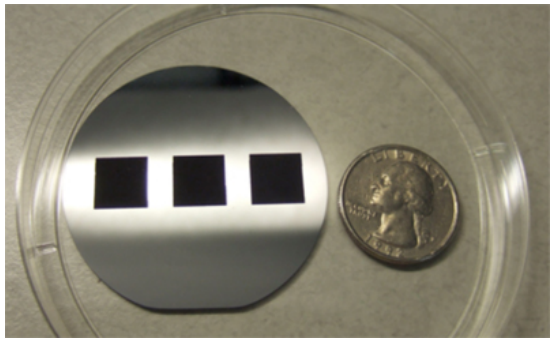


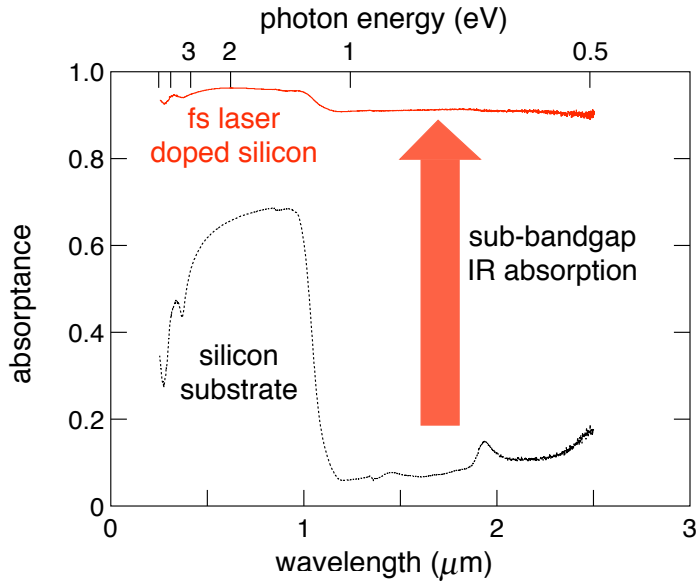

photon energy (eV)
3
2
1
0.5
1.0
0.8
0.6
0.4
0.2
0
absorptance
fs laser
doped silicon
sub-bandgap
IR absorption
silicon
substrate
0
1
2
3
wavelength (μm)

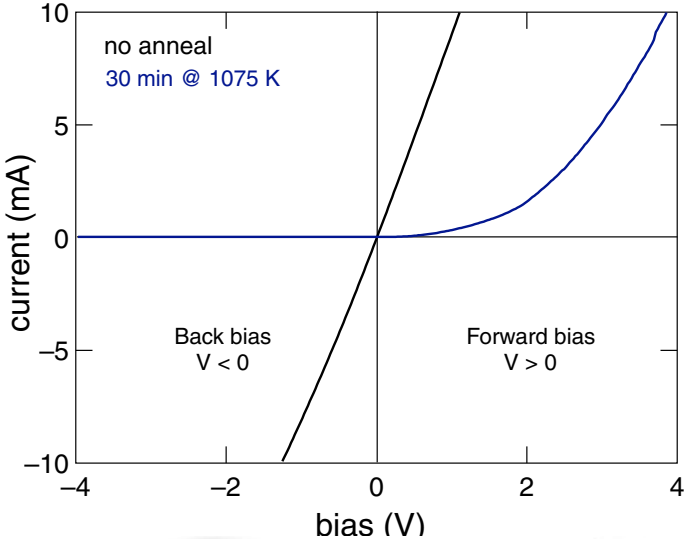

10
5
0
−5
−10
current (mA)
no anneal
30 min @ 1075 K
Back bias
V < 0
Forward bias
V > 0
−4
−2
0
2
4
bias (V)

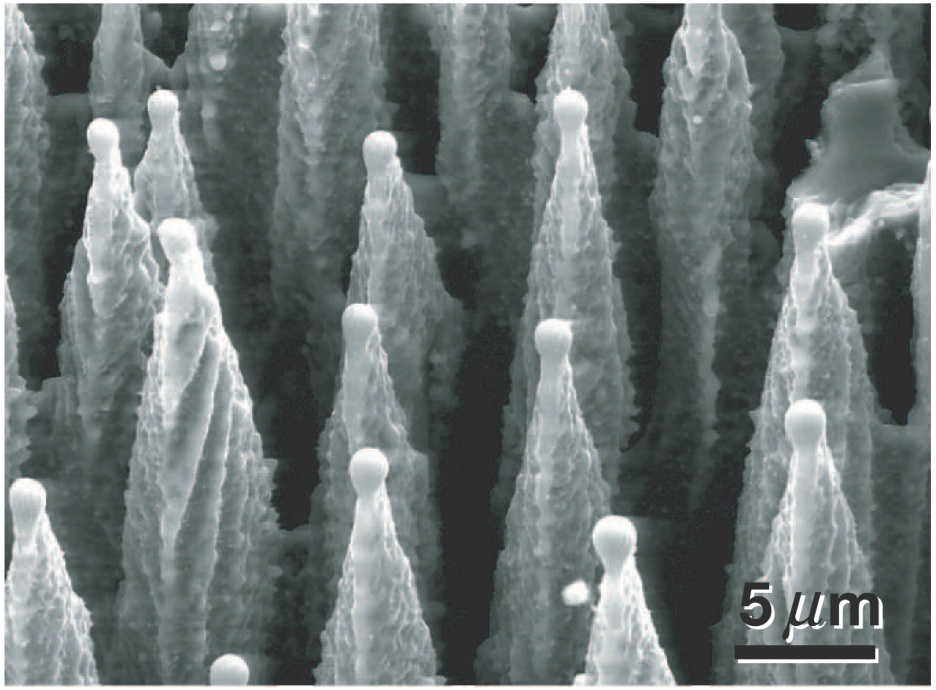

5 μm

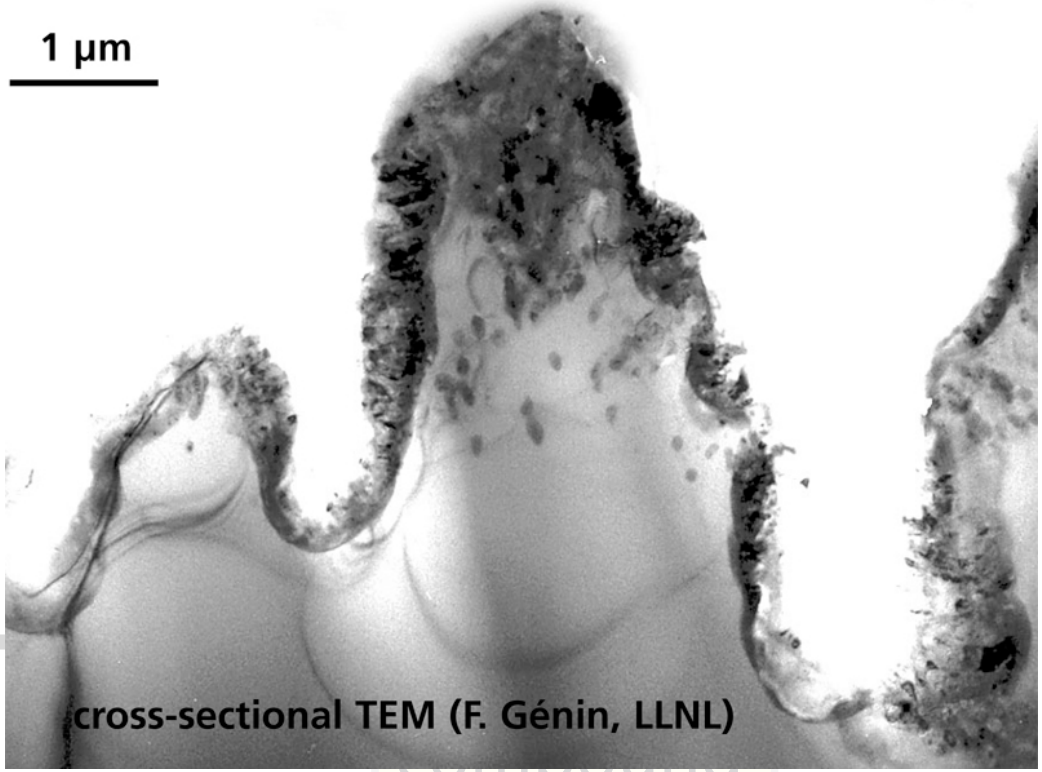
Sulfur
compound

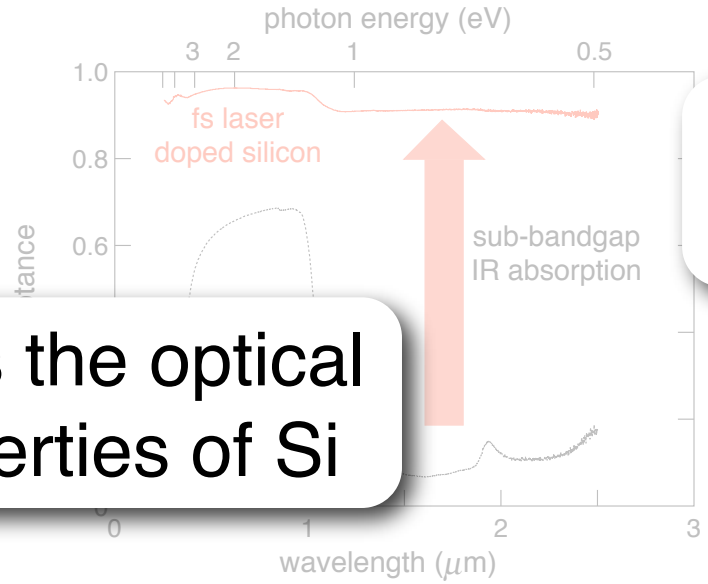



photon energy (eV)
3
2
1
0.5
1.0
0.8
0.6
0.4
0.2
0
absorptance
fs laser
doped silicon
sub-bandgap
IR absorption
silicon
substrate
0
1
2
3
wavelength (μm)

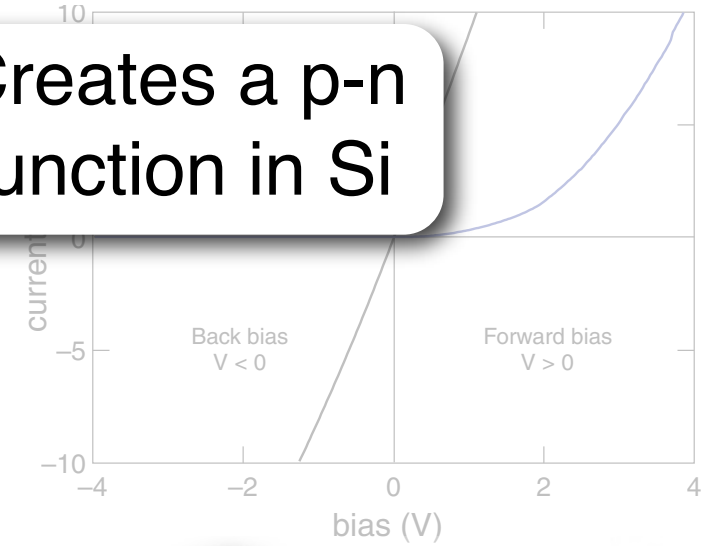

10
5
0
−5
−10
current (mA)
no anneal
30 min @ 1075 K
Back bias
V < 0
Forward bias
V > 0
−4
−2
0
2
4
bias (V)


5 μm

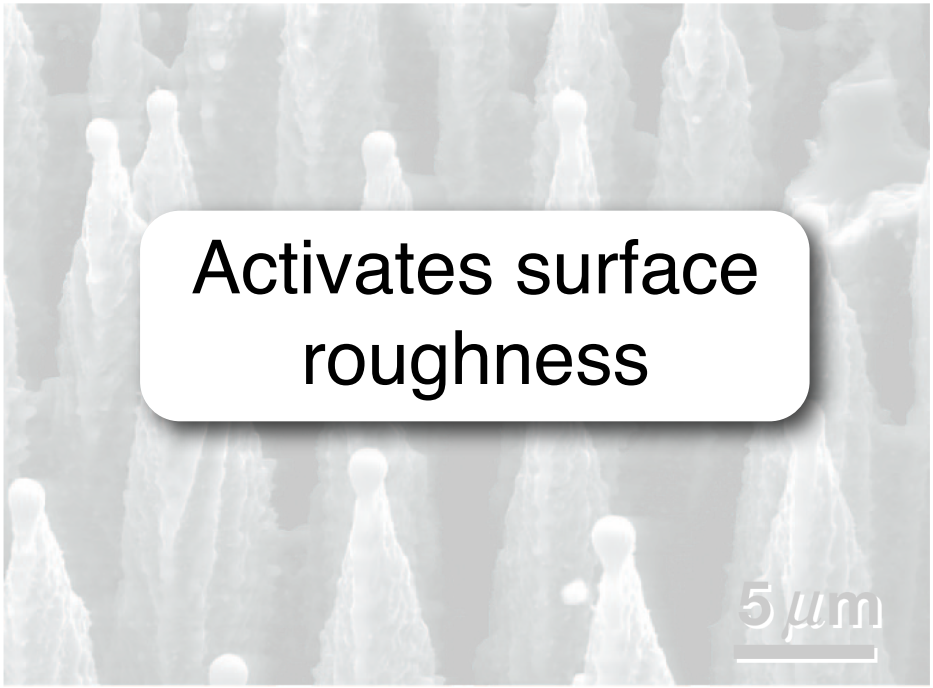

1 μm
cross-sectional TEM (F. Génin, LLNL)



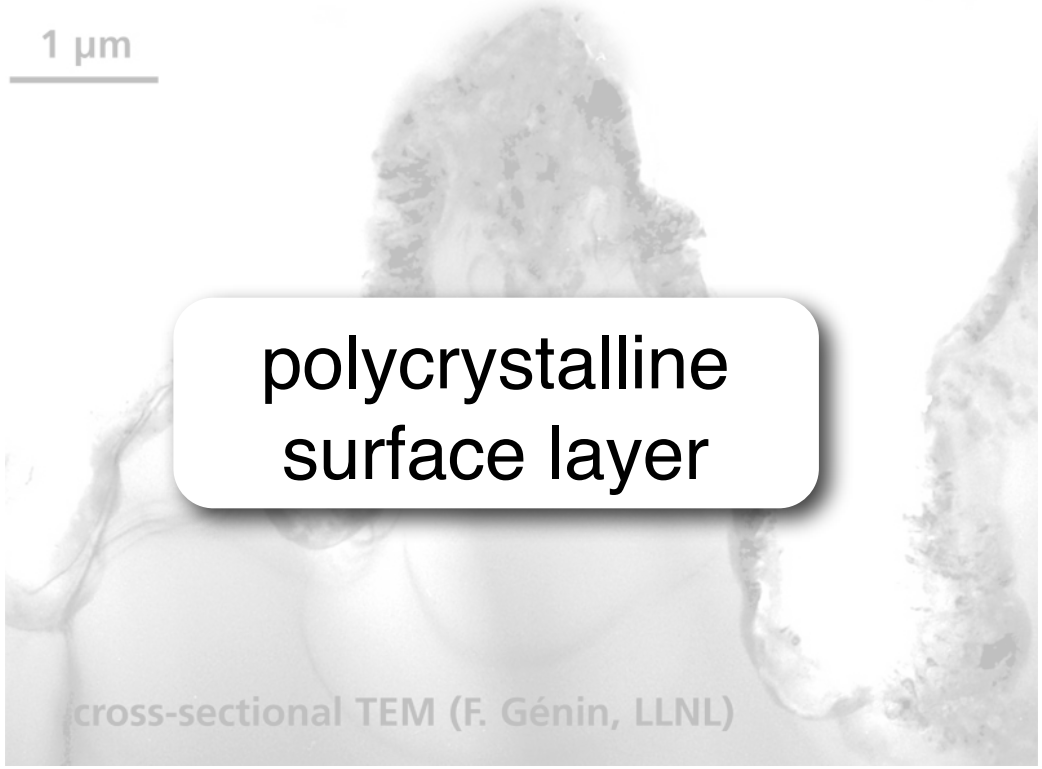
Alters the optical properties of Si



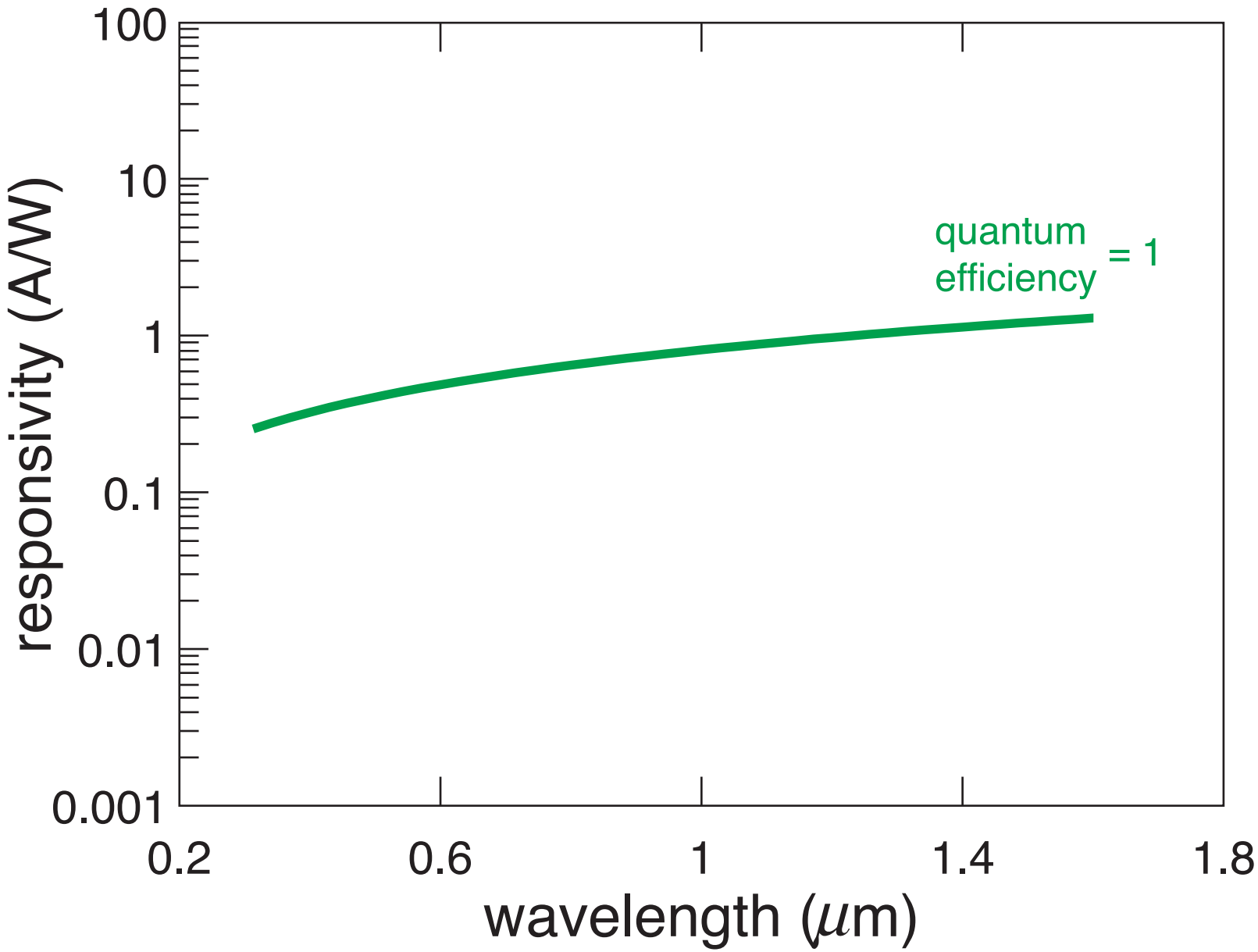
Creates a p-n junction in Si

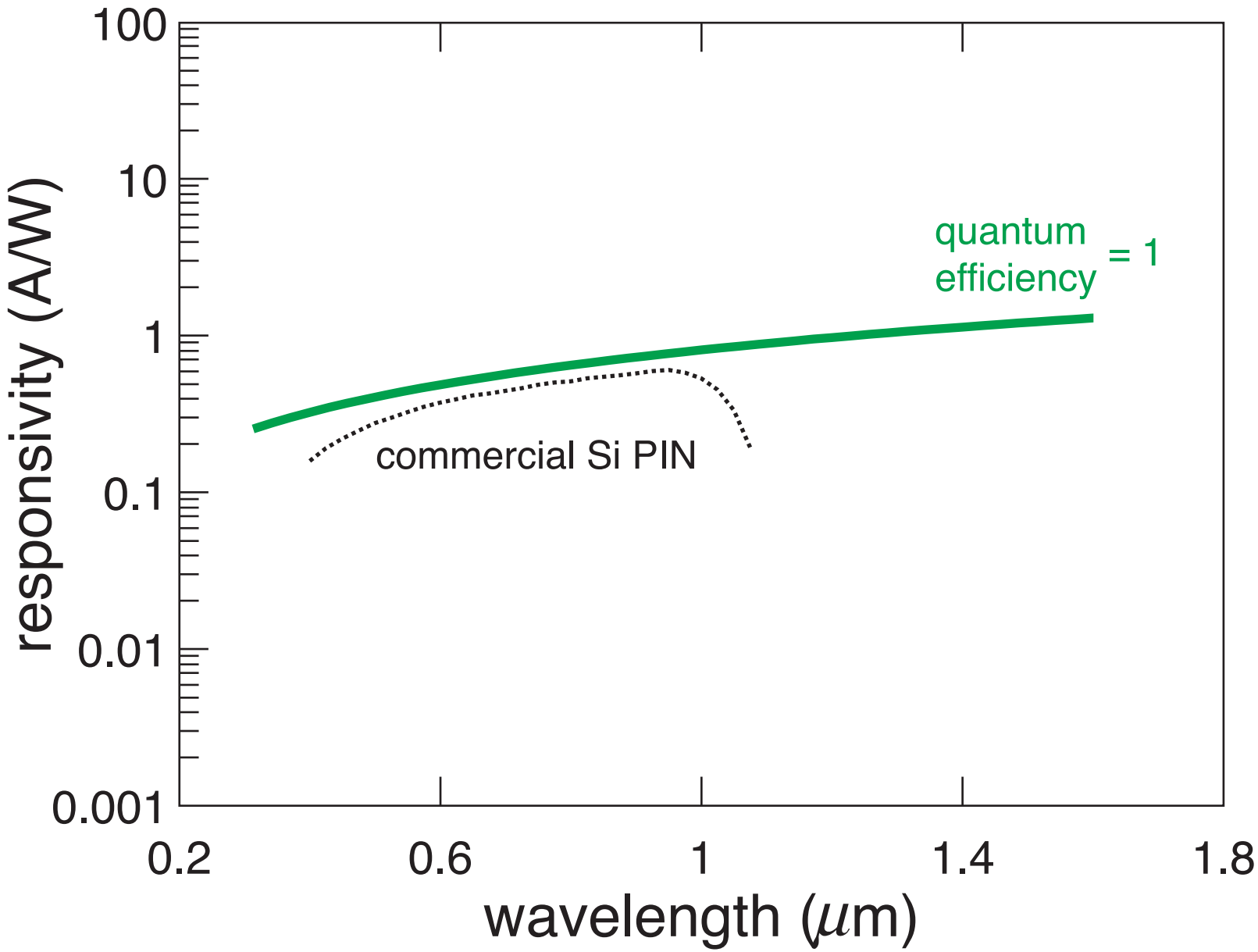


Activates surface roughness

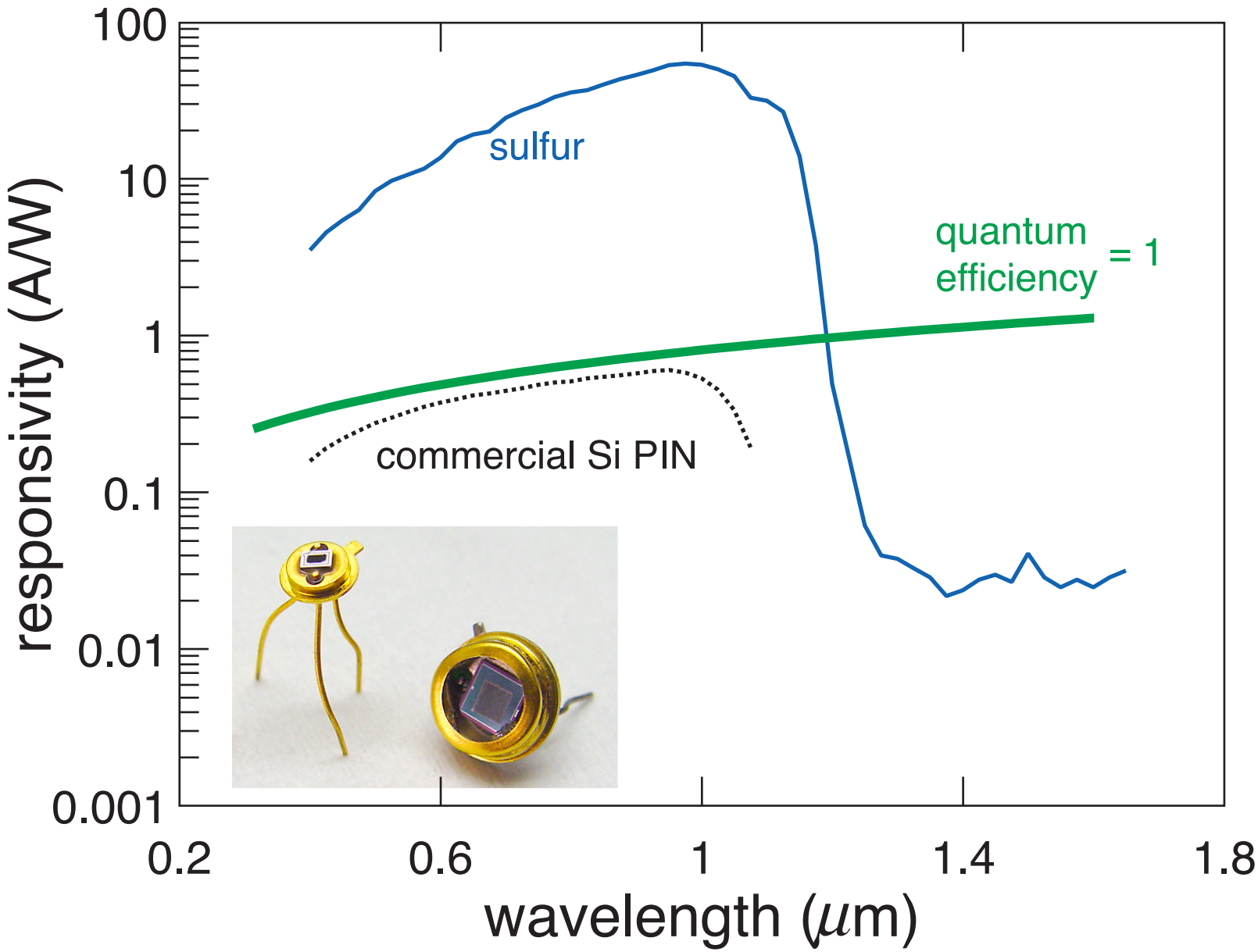


polycrystalline surface layer

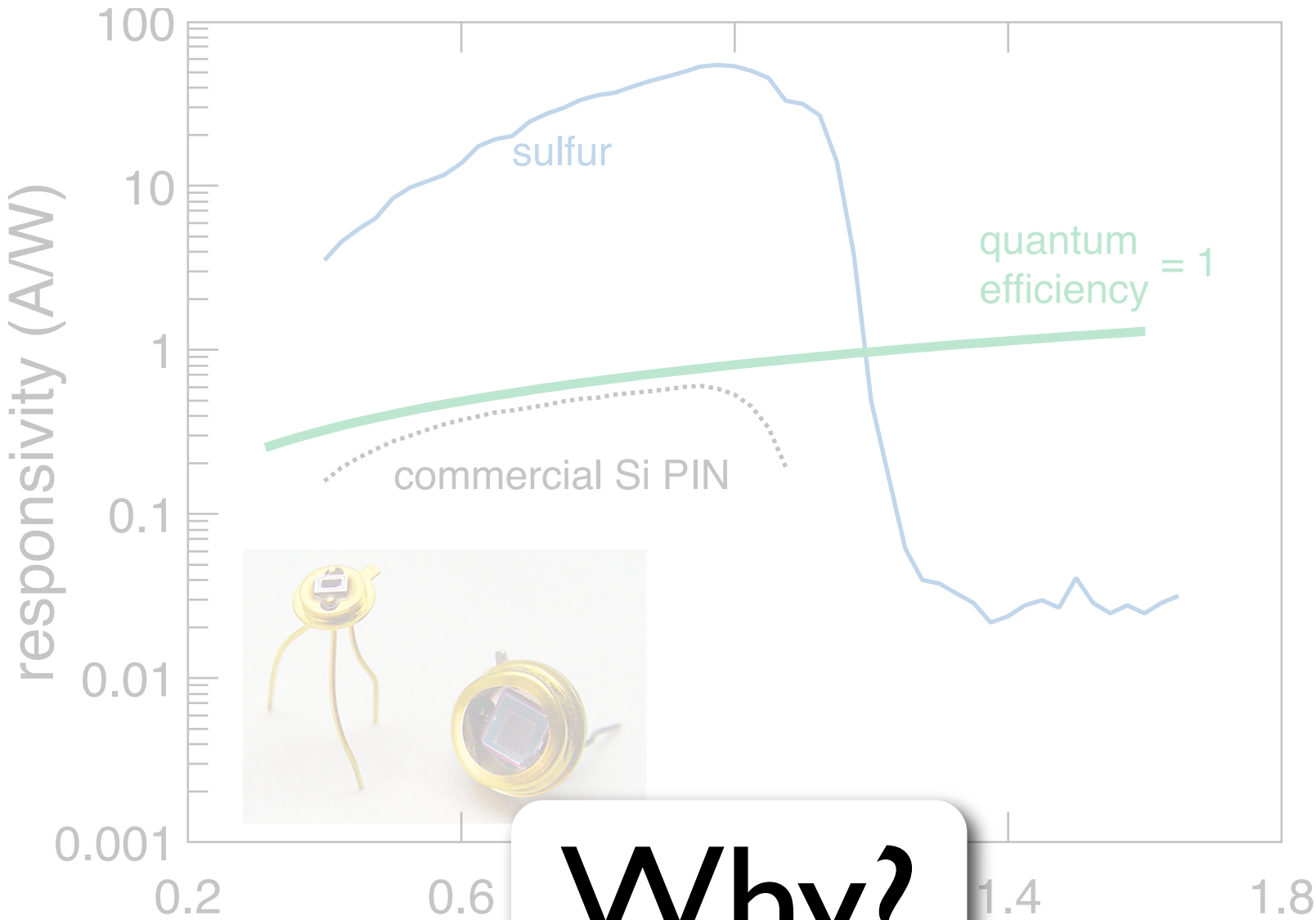

100
10
1
0.1
0.01
0.001
responsivity (A/W)
quantum
efficiency
= 1
0.2
0.6
1
1.4
1.8
wavelength (μm)


100
10
1
0.1
0.01
0.001
responsivity (A/W)
quantum
efficiency
= 1
commercial Si PIN
0.2
0.6
1
1.4
1.8
wavelength (μm)

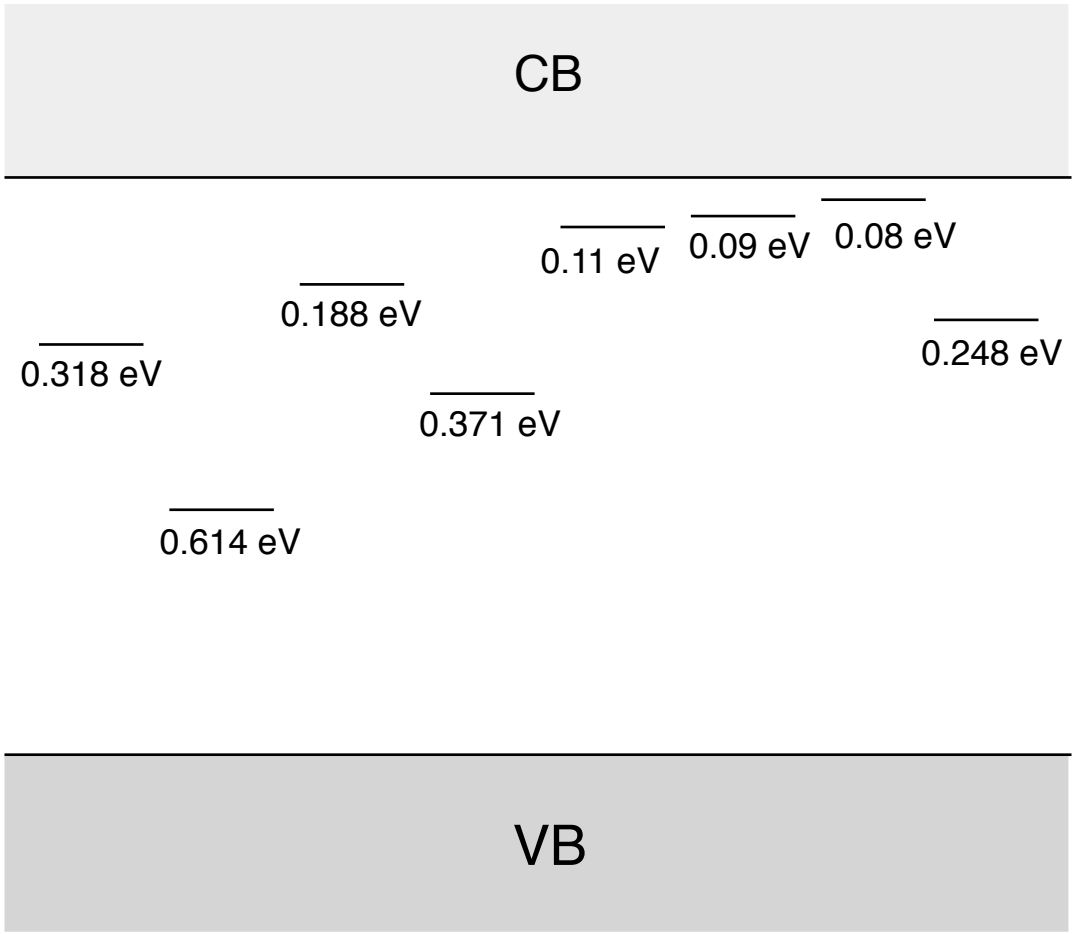
Laser-doping extends silicon's reach



Laser-doping extends silicon's reach



Why?



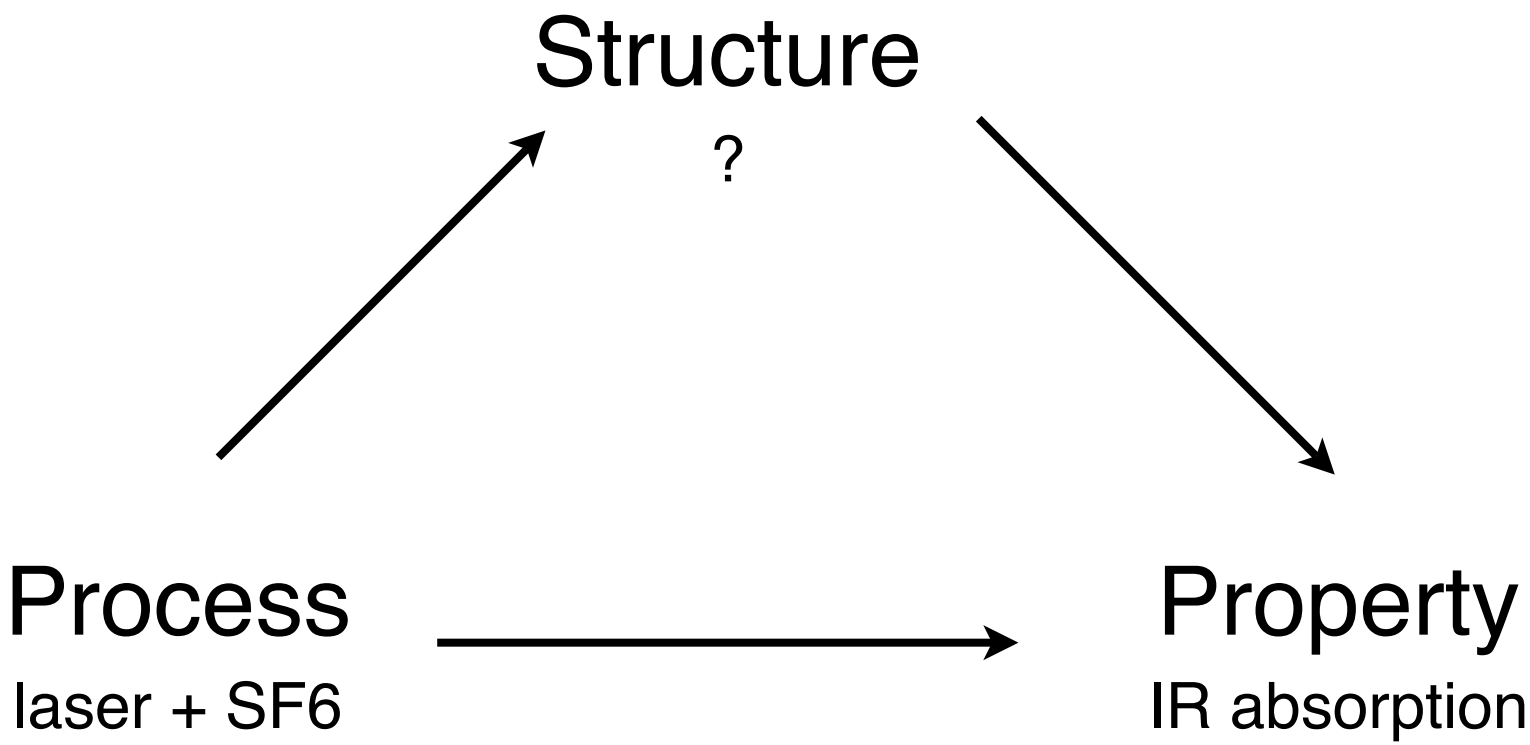
Janzén et al. , Phys. Rev. B 29, 1907 (1984)

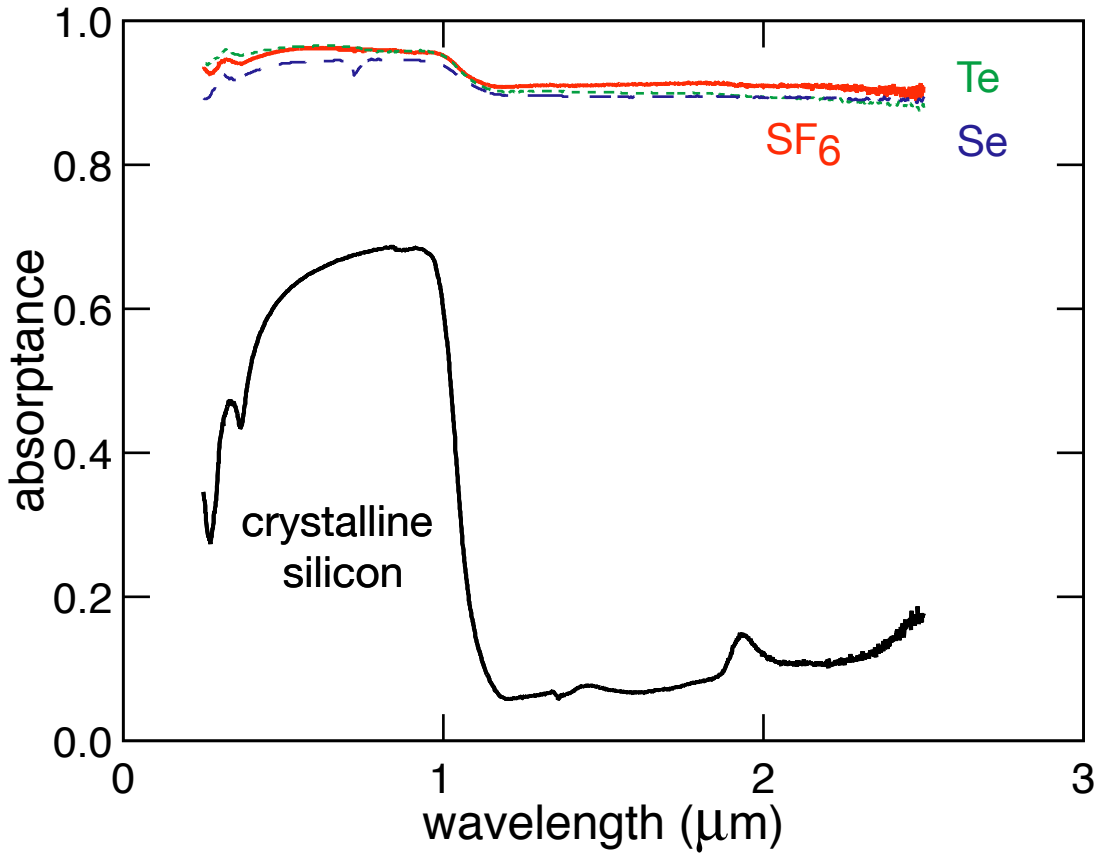
Hypothesis: non-equilibrium doping yields impurity band

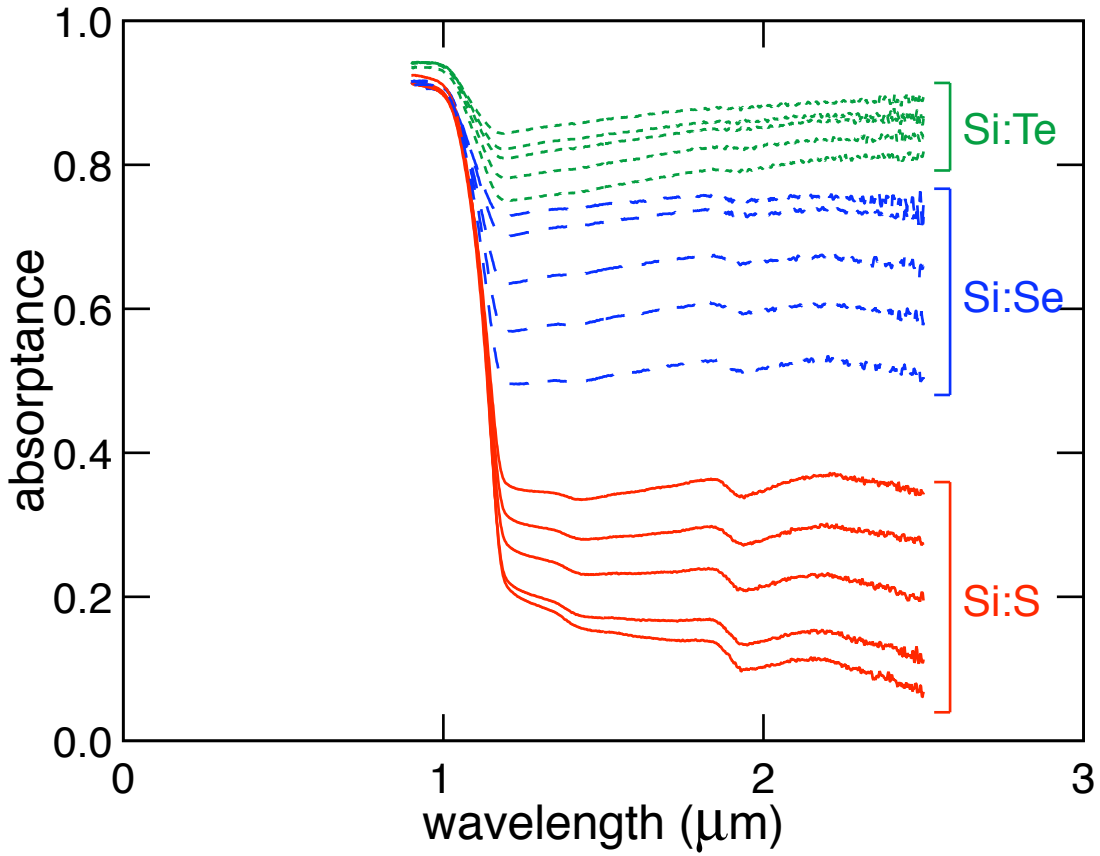
Process → Property

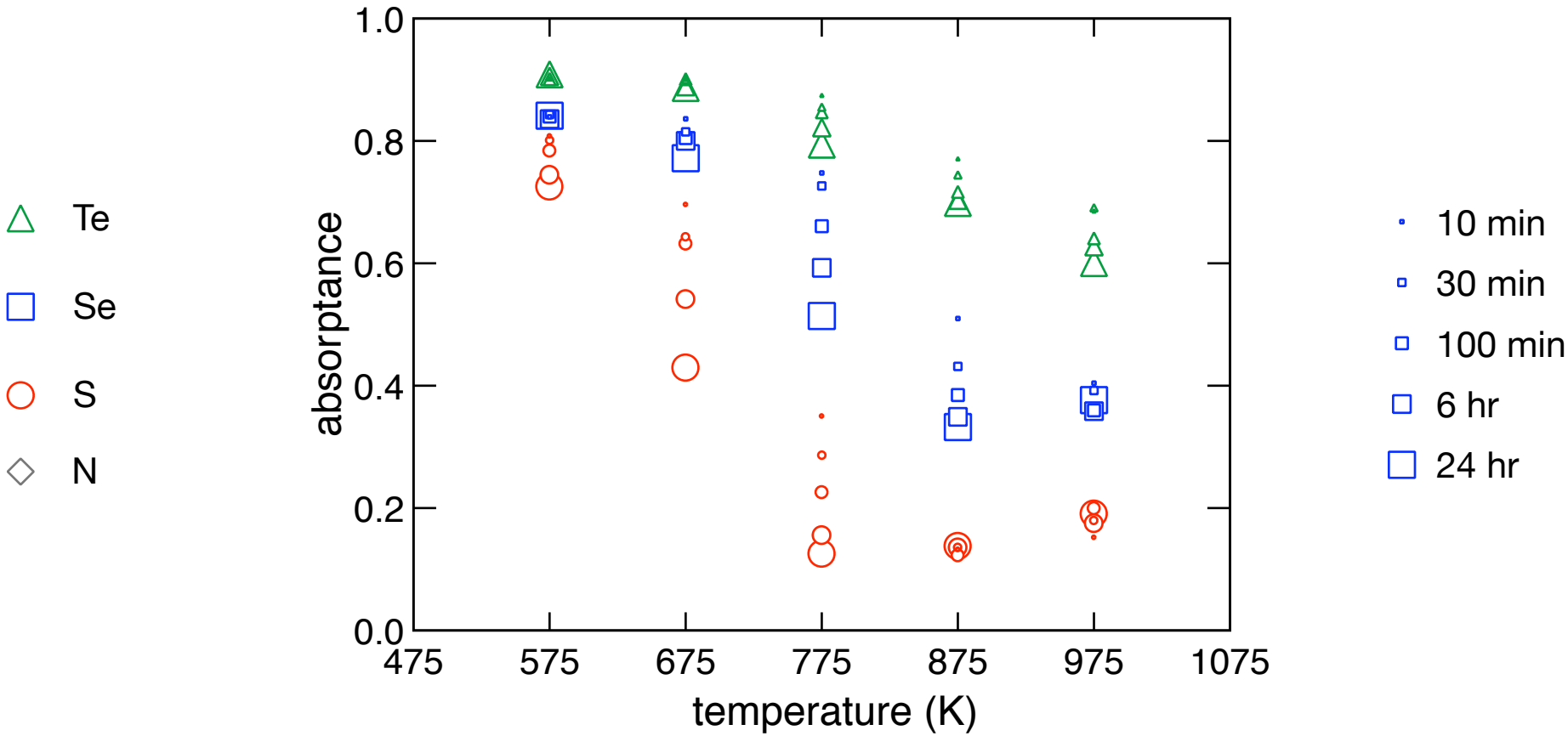
laser + SF6

IR absorption

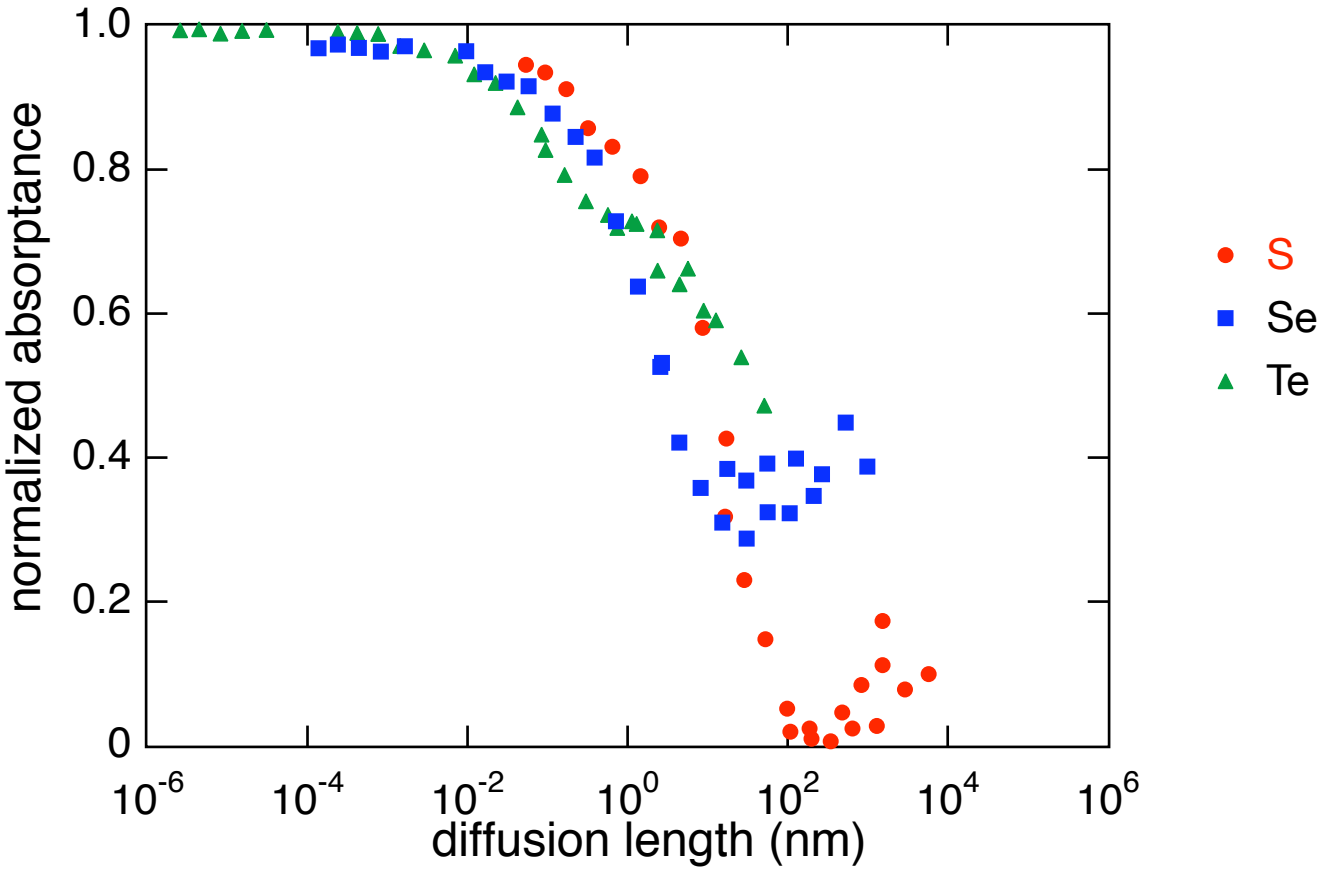

Structure
?
Process
laser + SF6
Property
IR absorption


1.0
0.8
0.6
0.4
0.2
0.0
absorptance
0
1
2
3
wavelength (μm)
Te
SF6
Se
crystalline
silicon

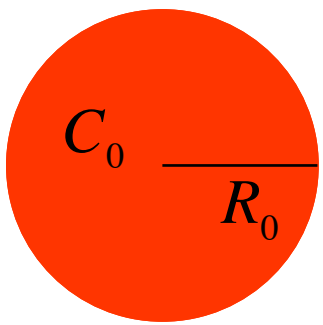

1.0
0.8
0.6
0.4
0.2
0.0
absorptance
0
1
2
3
wavelength (μm)
Si:Te
Si:Se
Si:S

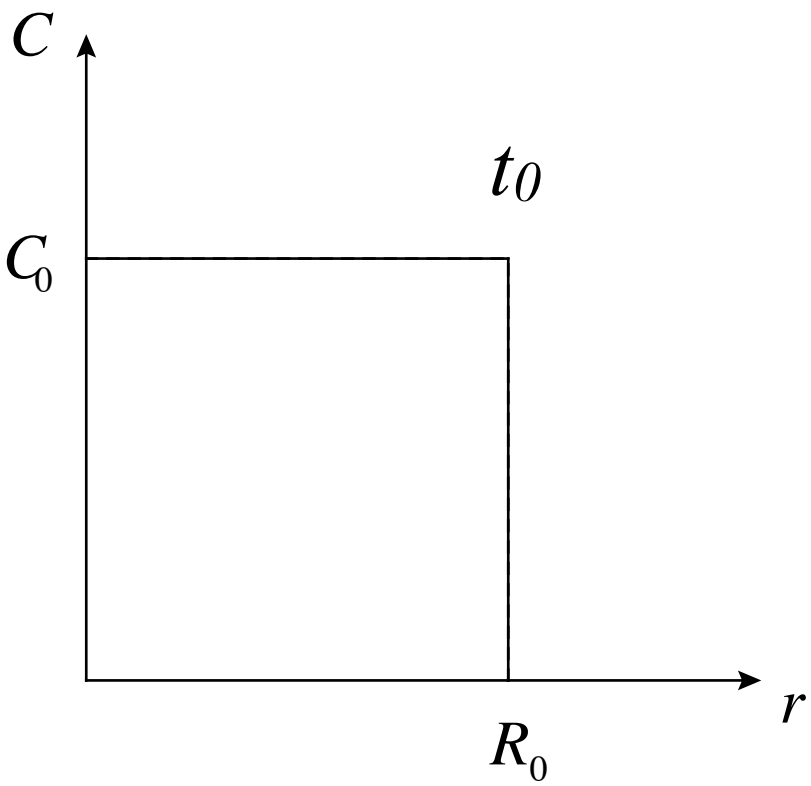


$$\text{diffusion length} = \sqrt{D_i t} = f(T,t)$$


1.0
0.8
0.6
0.4
0.2
0
normalized absorptance
10^{-6}
10^{-4}
10^{-2}
10^{0}
10^{2}
10^{4}
10^{6}
diffusion length (nm)
S
Se
Te

Could this diffusion-related drop in absorptance be governed by grain size?





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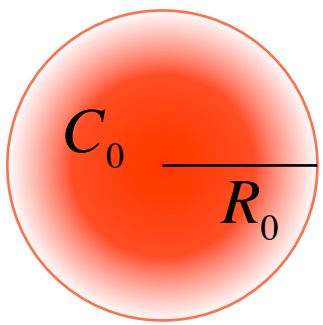

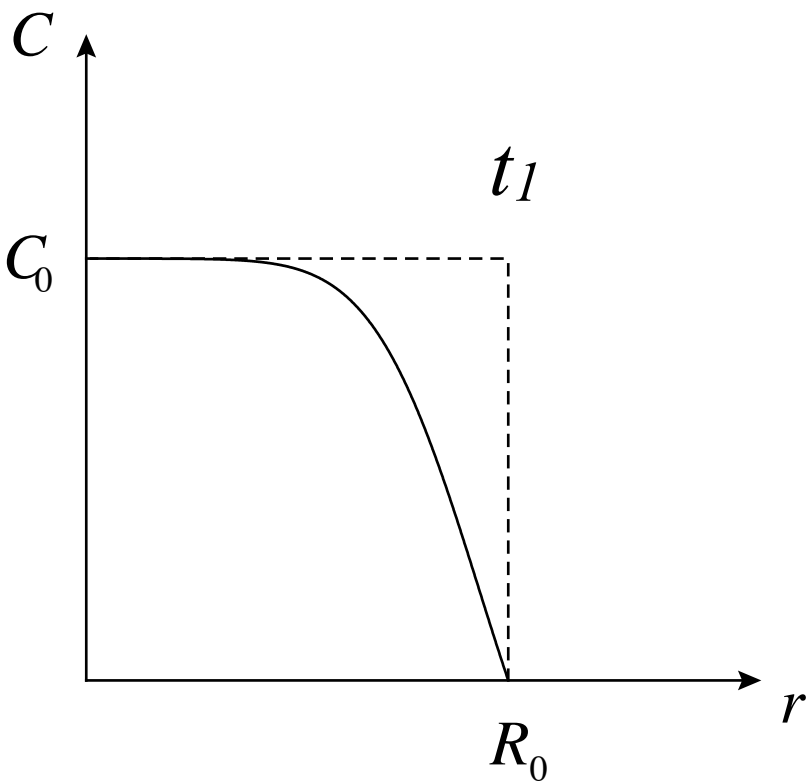

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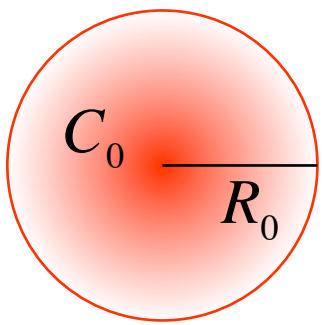
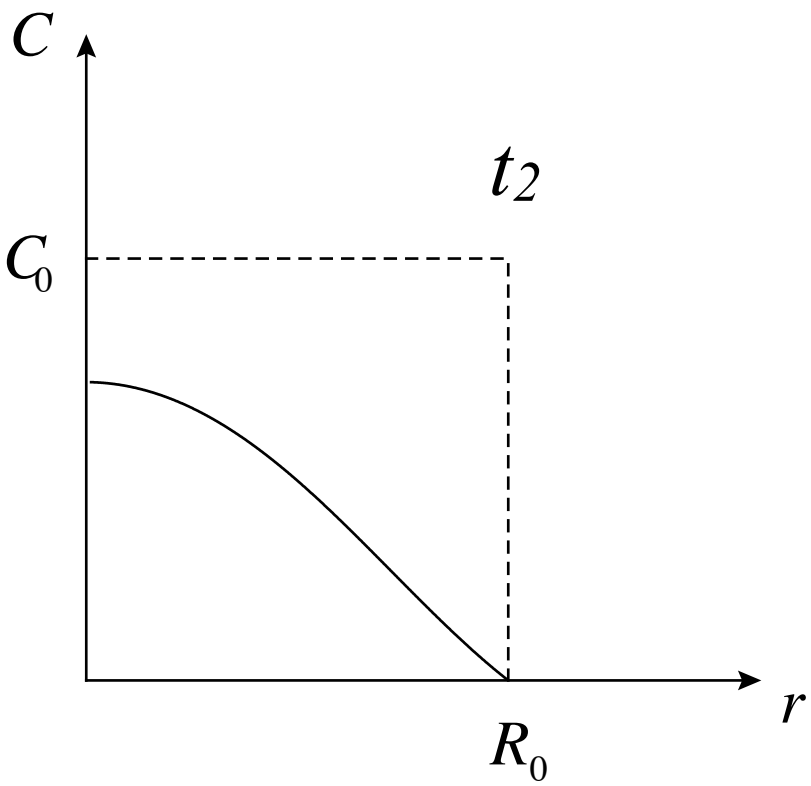
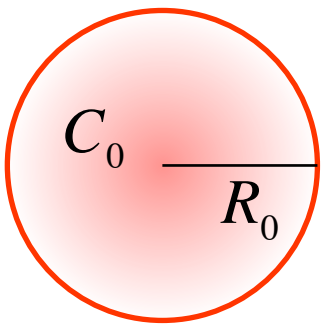
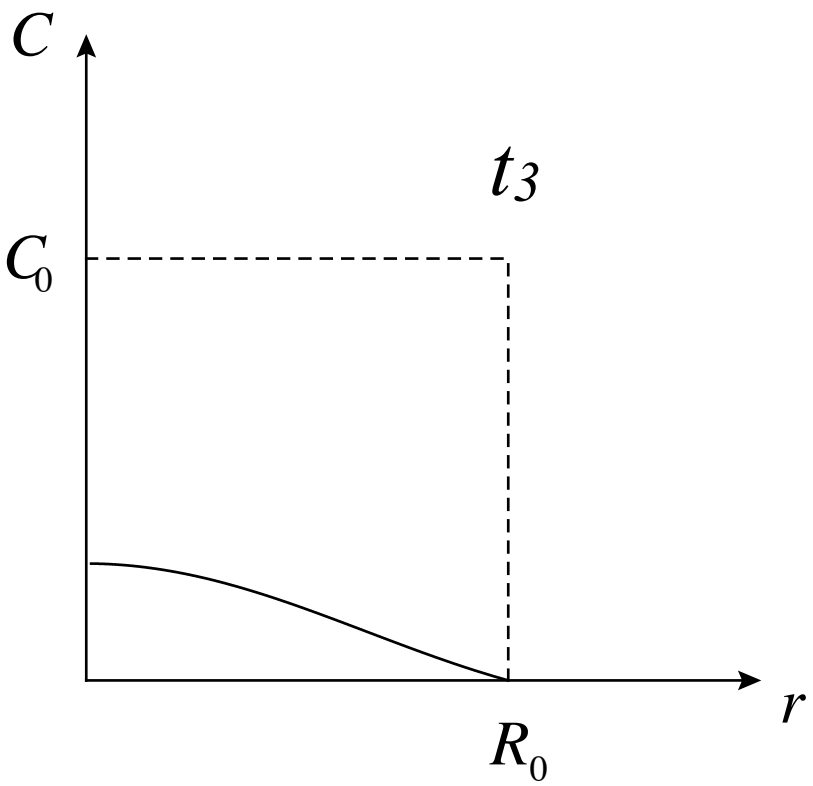




Could this diffusion-related drop in absorptance be governed by grain size?





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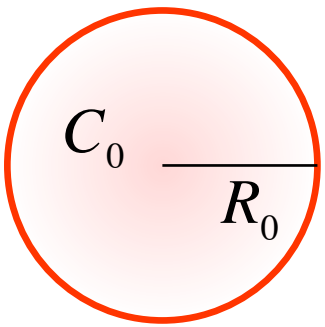
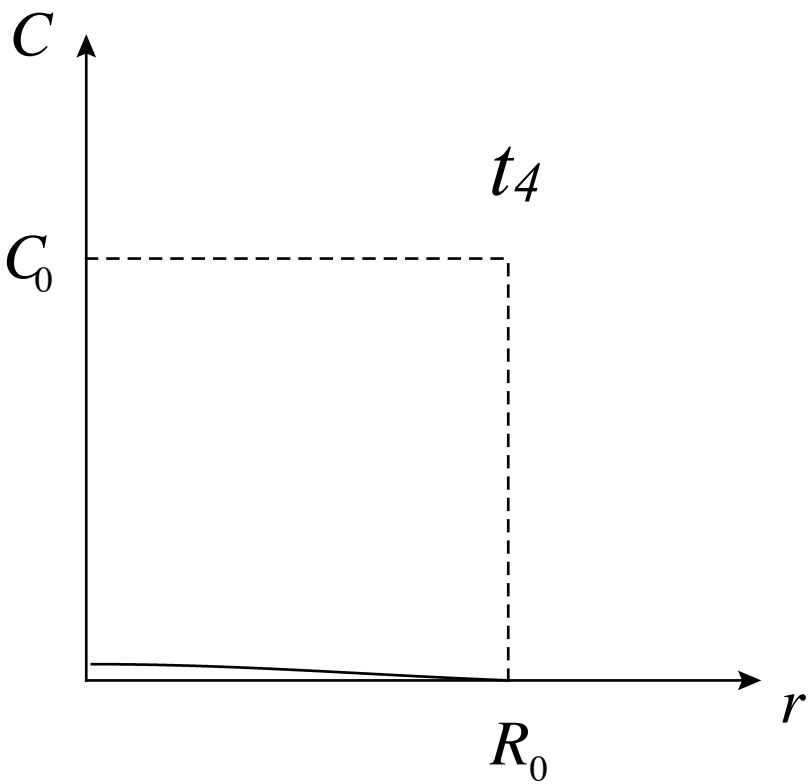
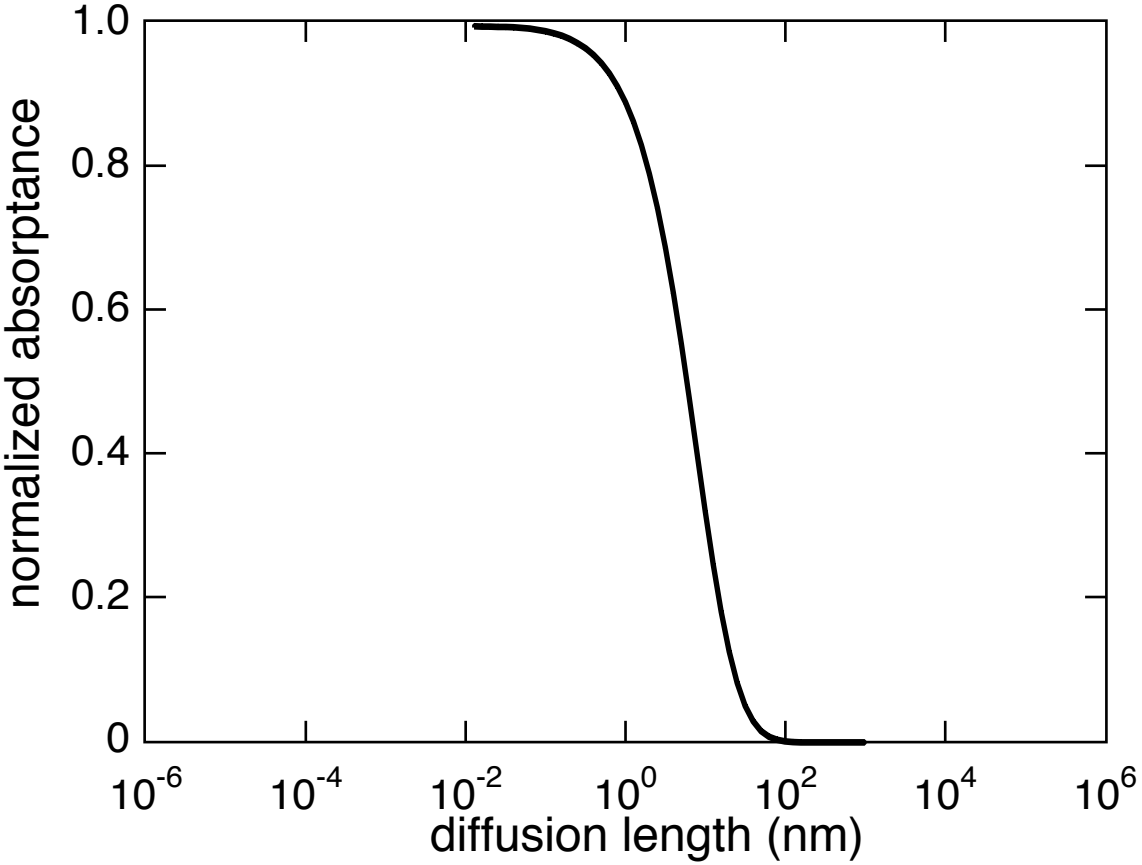
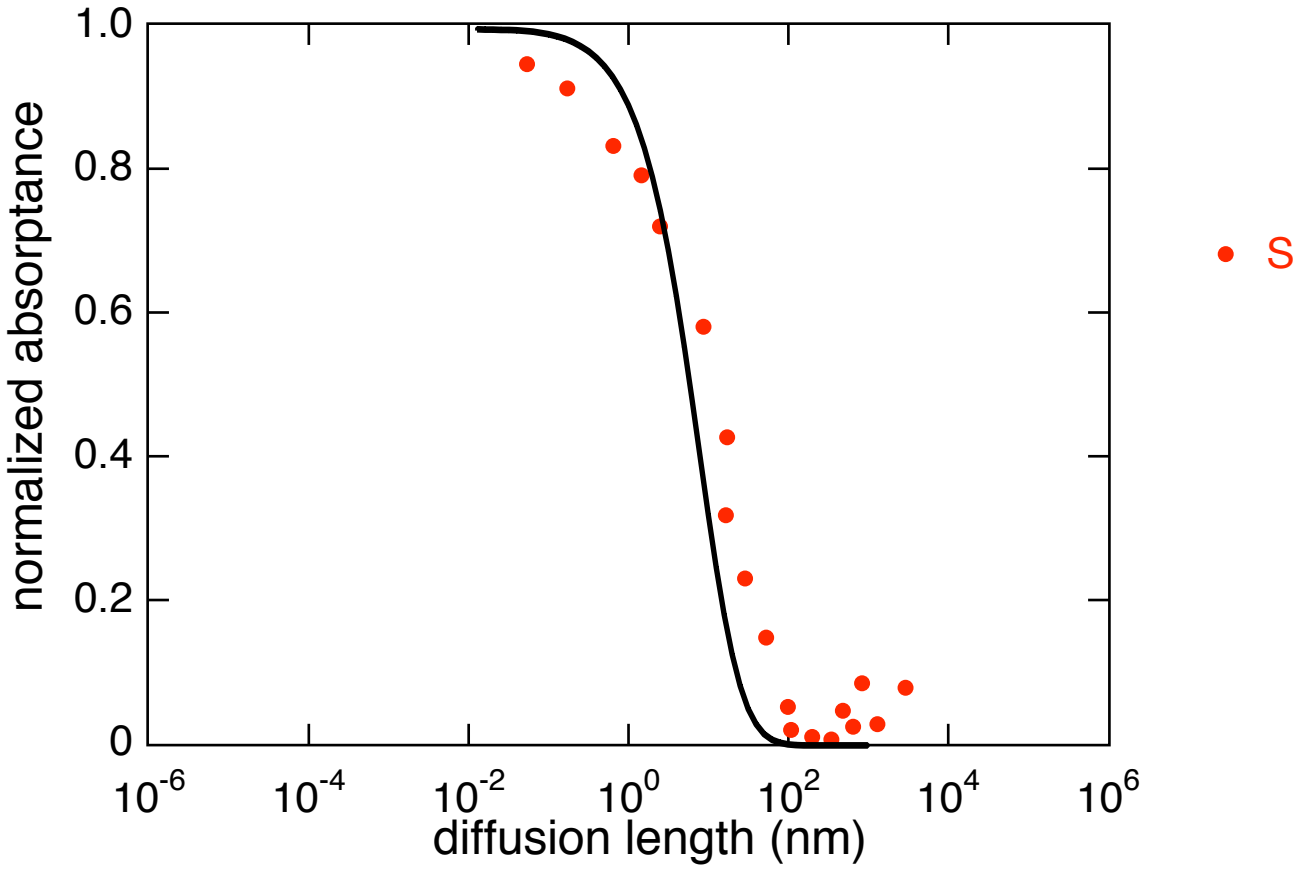
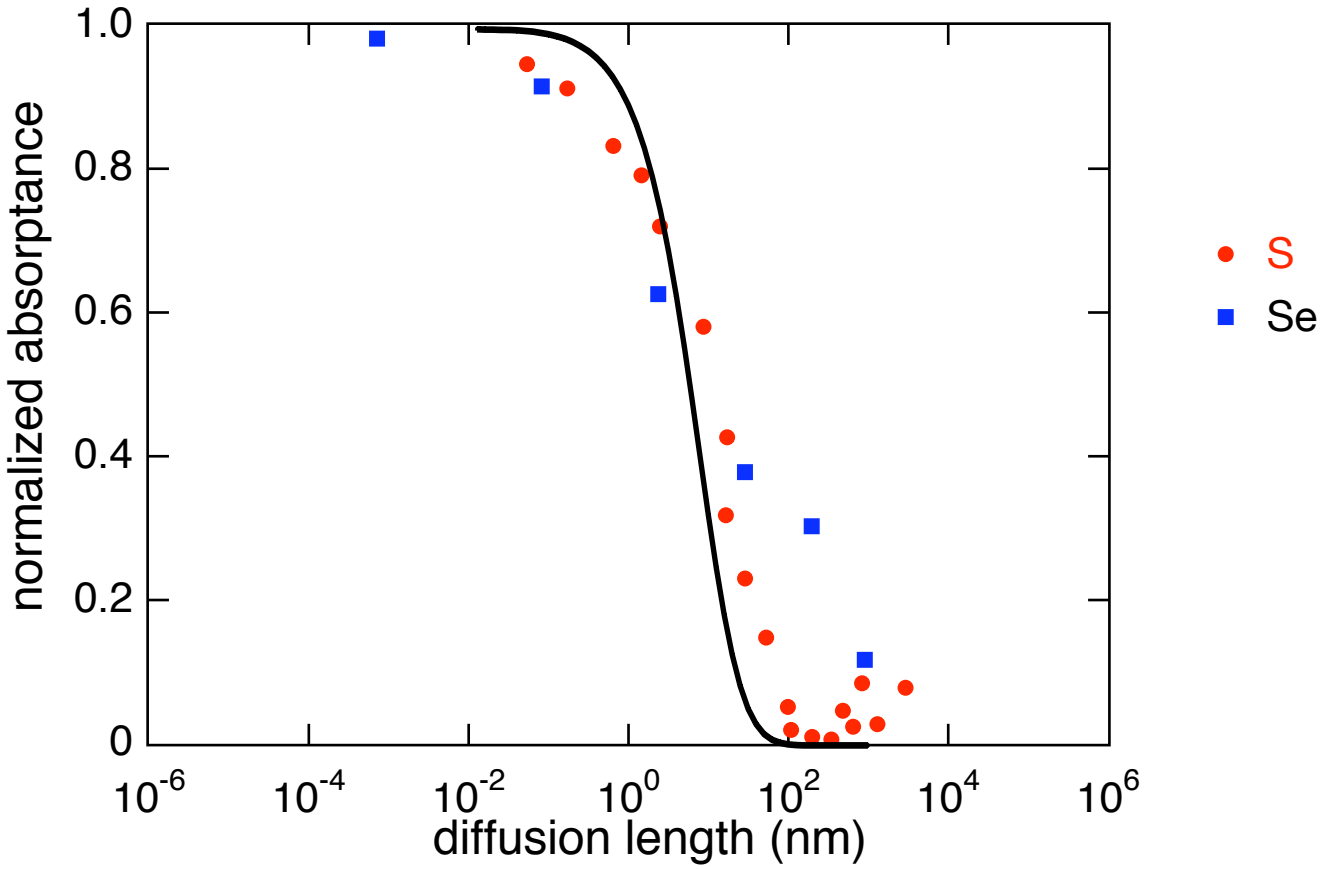
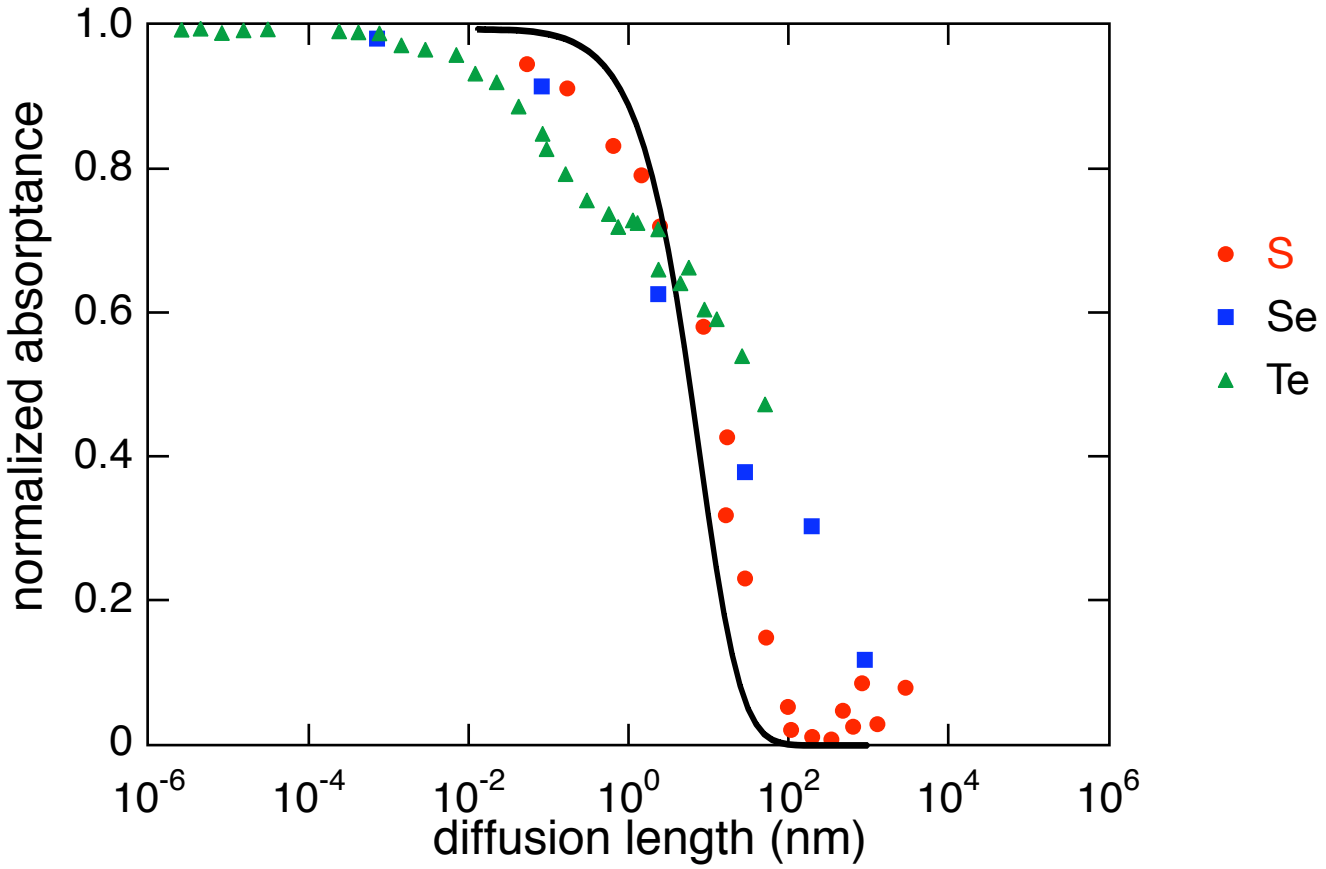




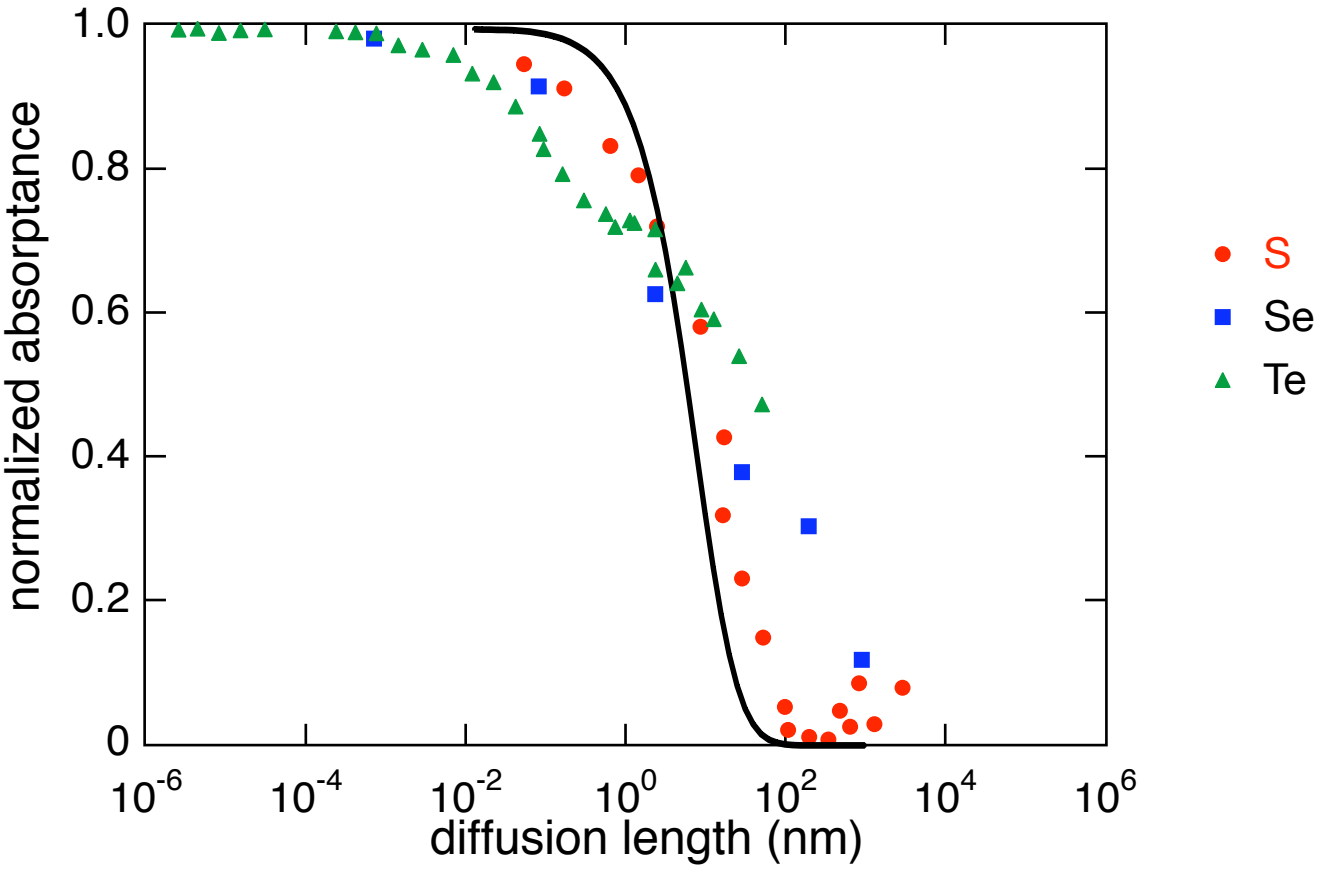

1.0
0.8
0.6
0.4
0.2
0
normalized absorptance
10^{-6}
10^{-4}
10^{-2}
10^{0}
10^{2}
10^{4}
10^{6}
diffusion length (nm)

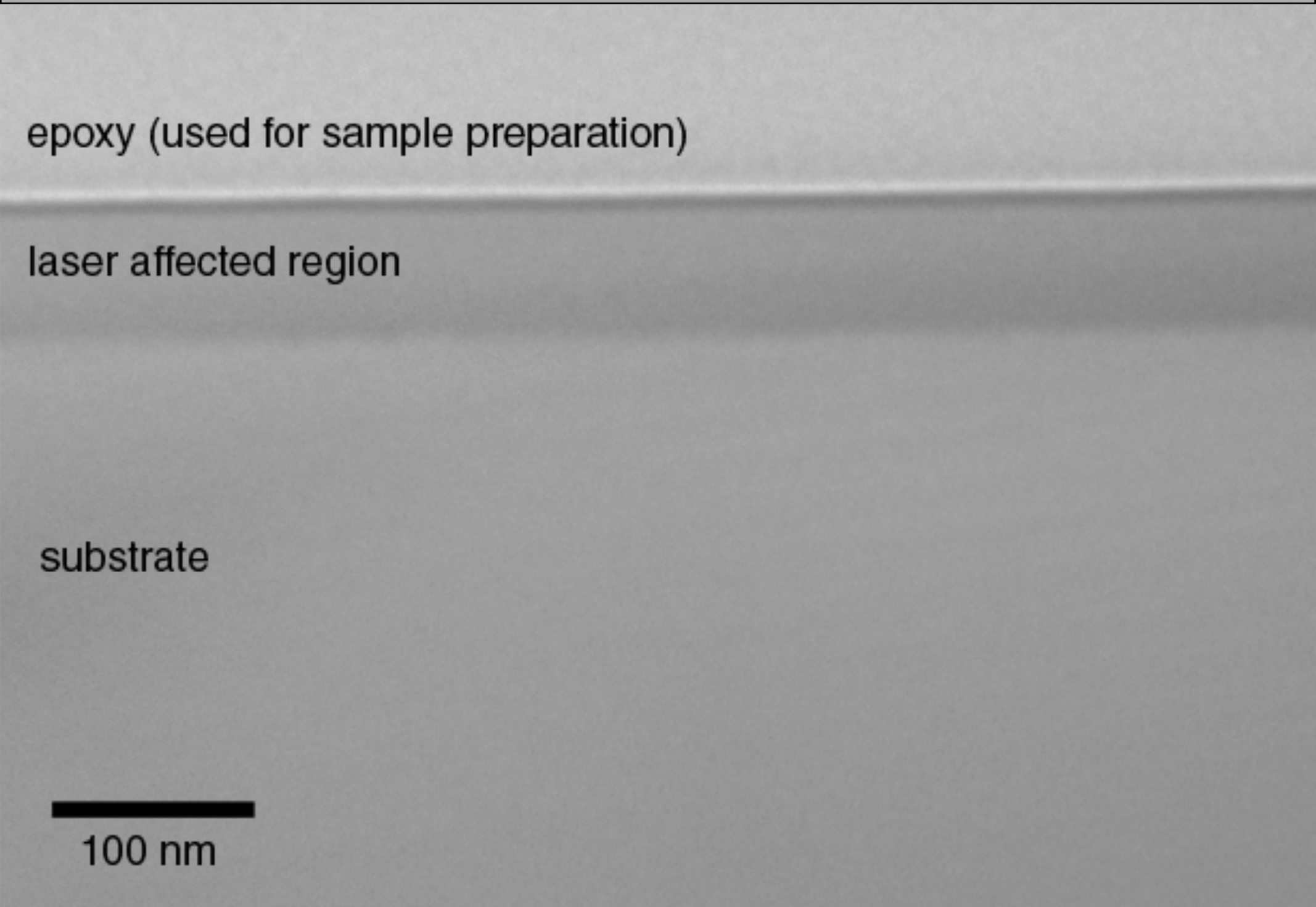

1.0
0.8
0.6
0.4
0.2
0
normalized absorptance
10^{-6}
10^{-4}
10^{-2}
10^{0}
10^{2}
10^{4}
10^{6}
diffusion length (nm)
S


1.0
0.8
0.6
0.4
0.2
0
normalized absorptance
10^{-6}
10^{-4}
10^{-2}
10^{0}
10^{2}
10^{4}
10^{6}
diffusion length (nm)
S
Se


1.0
0.8
0.6
0.4
0.2
0
normalized absorptance
10^{-6}
10^{-4}
10^{-2}
10^{0}
10^{2}
10^{4}
10^{6}
diffusion length (nm)
S
Se
Te

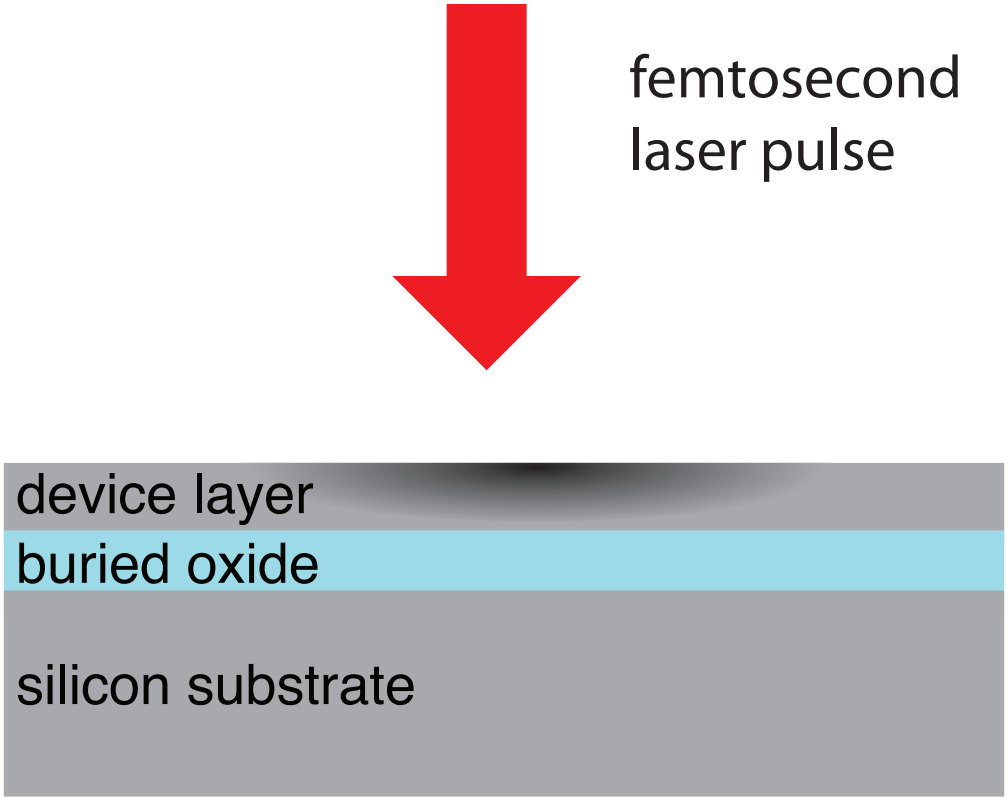
Conclusion: diffusion is a critical mechanism involved in deactivation of optical response



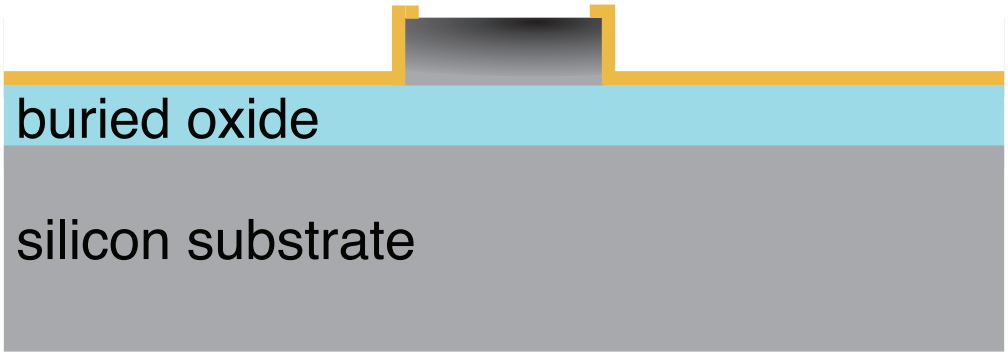

epoxy (used for sample preparation)
laser affected region
substrate
100 nm

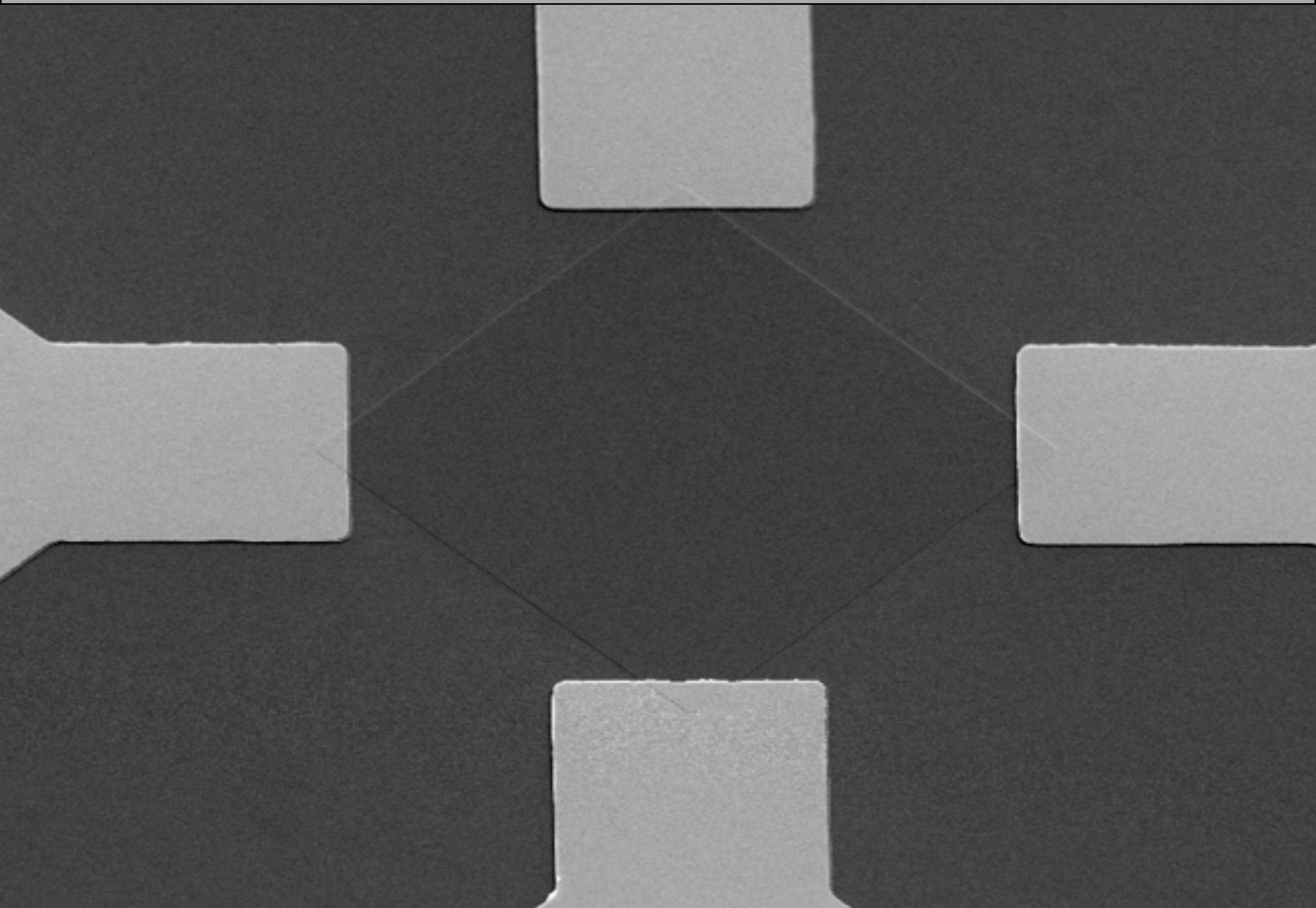
Isolate surface properties

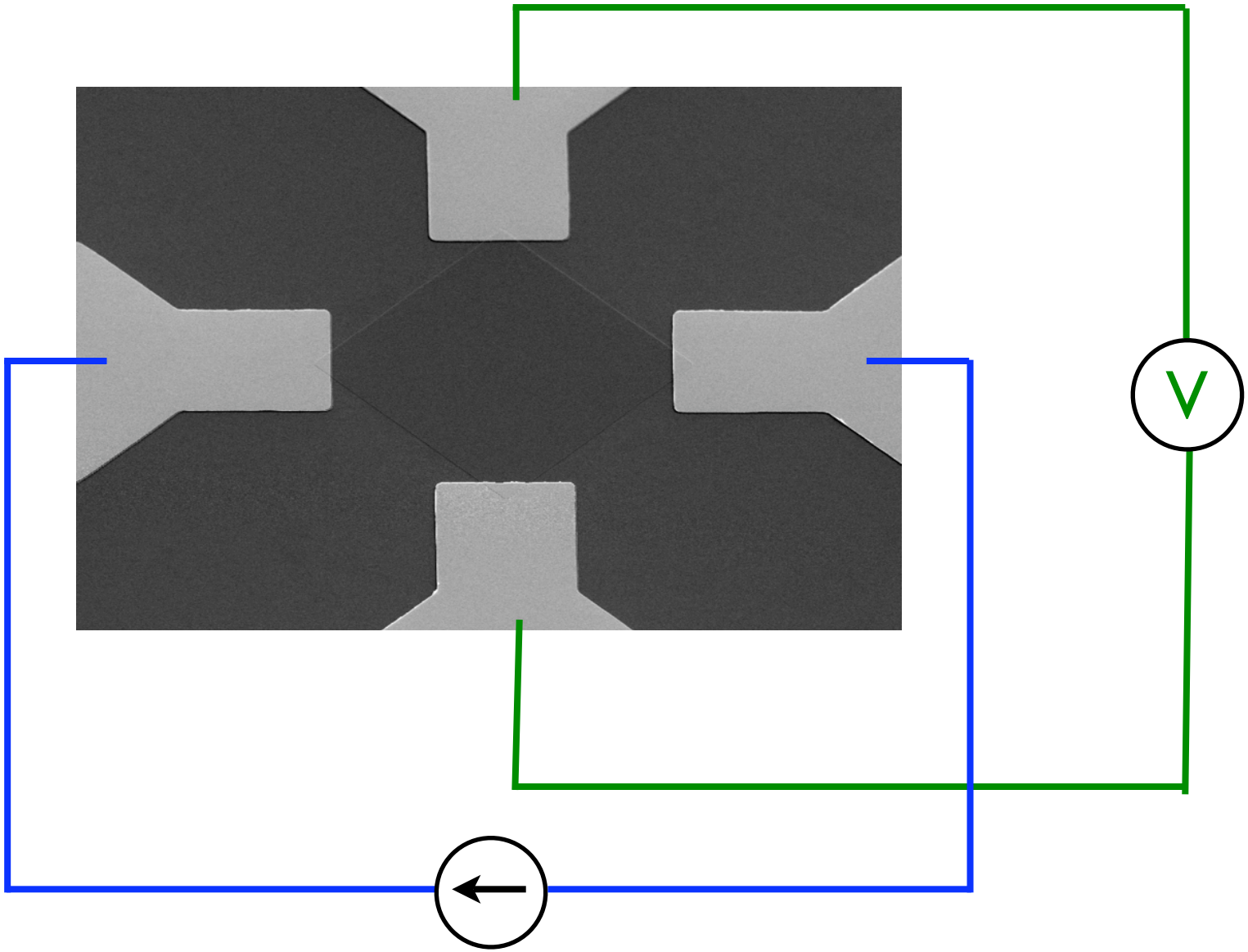
Isolate surface properties



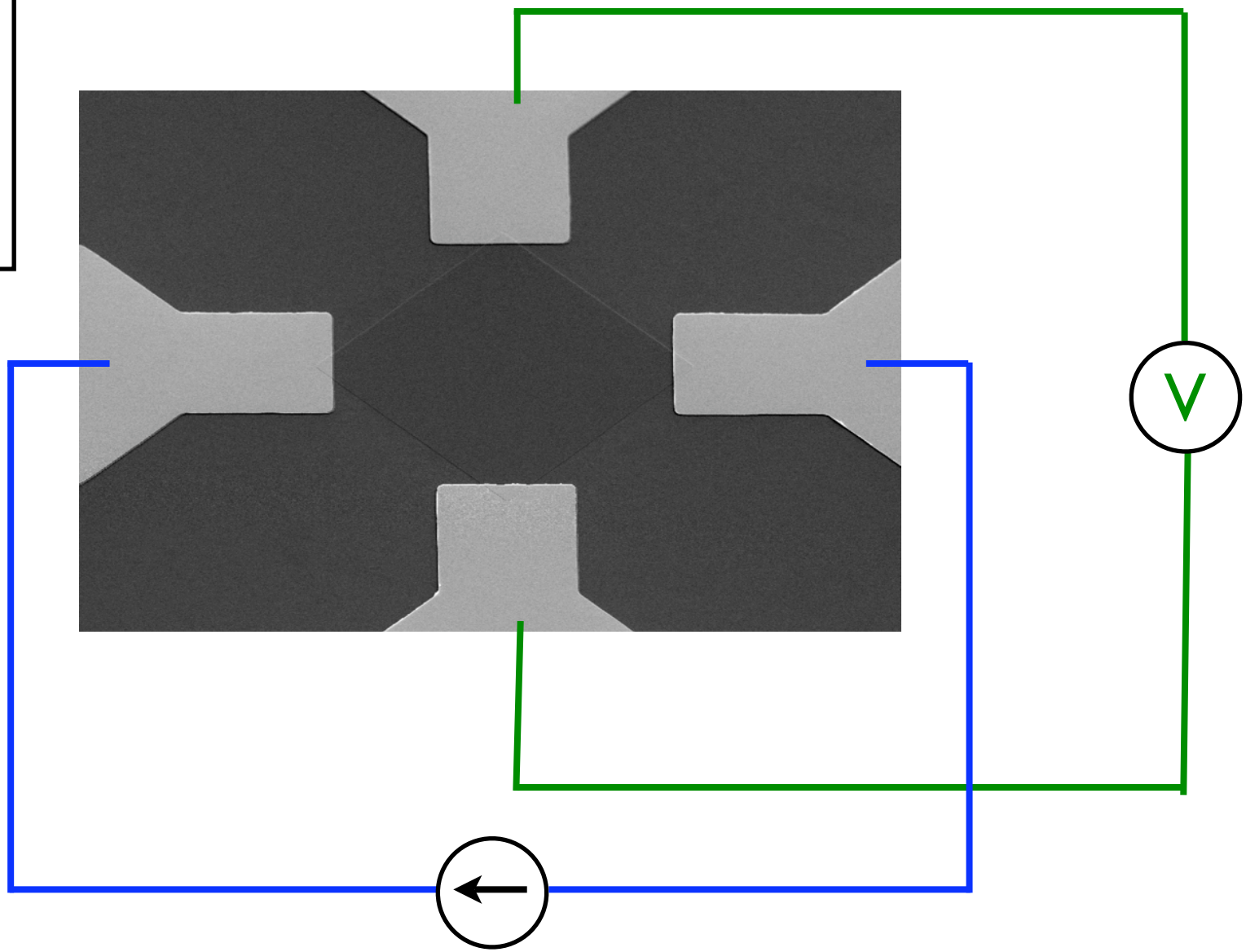
Isolate surface properties





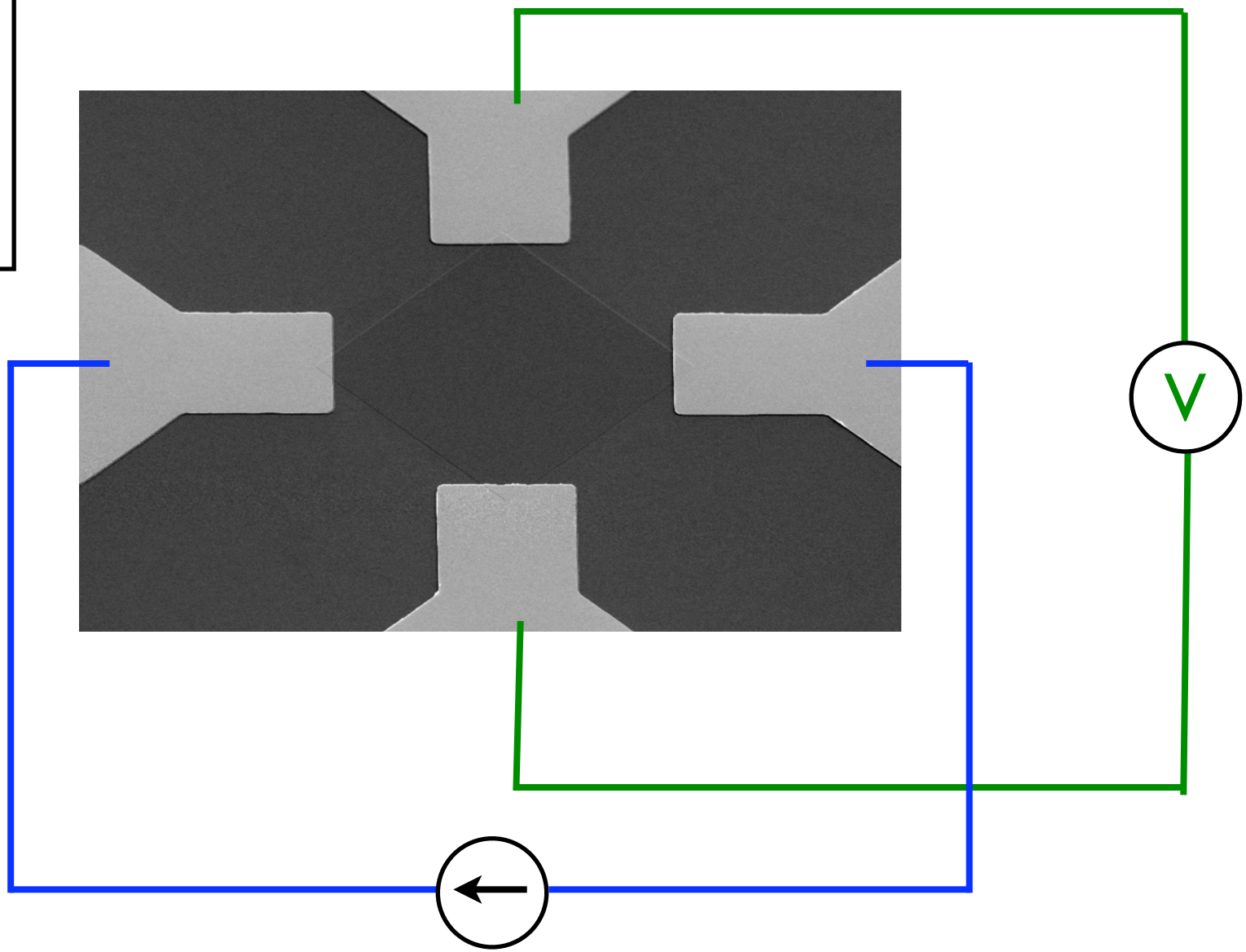

V

$$n = \frac{IB}{qdV}$$

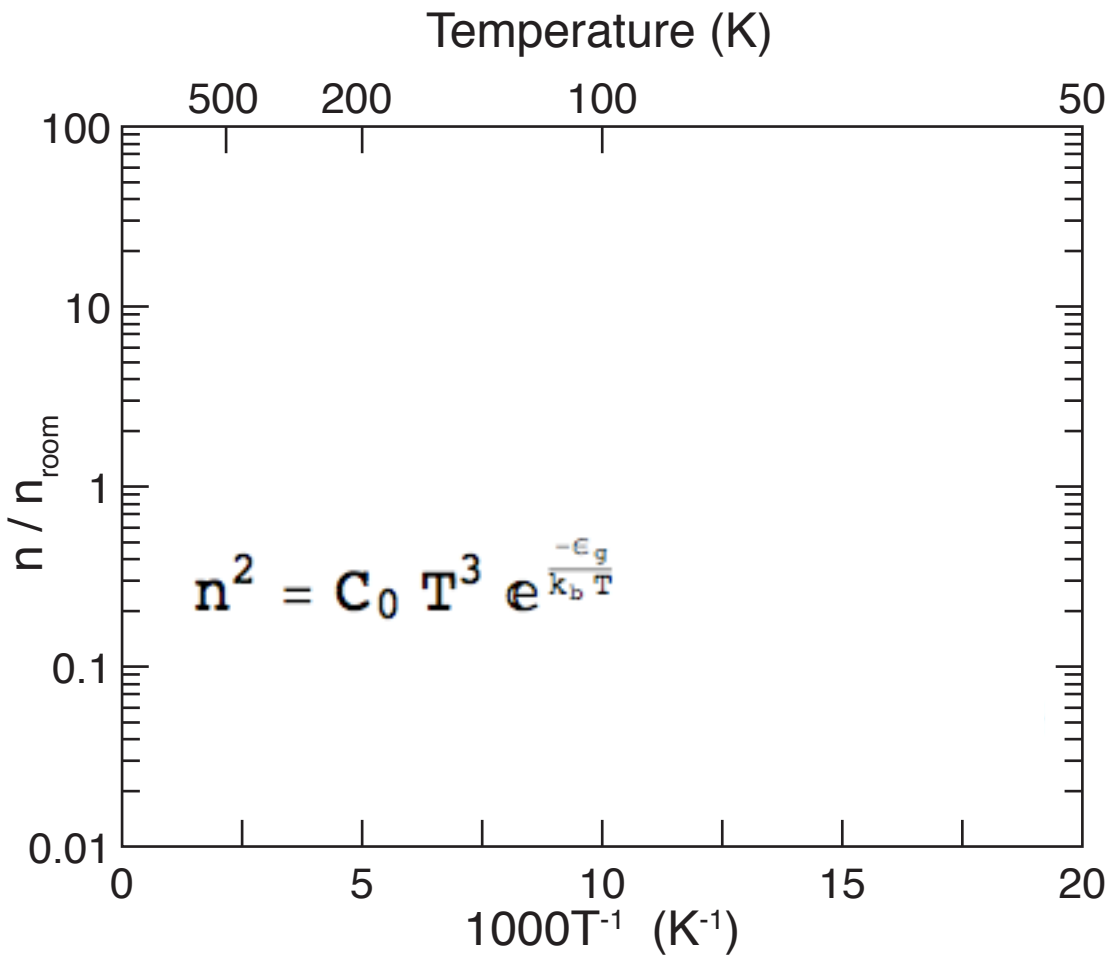


$$n = \frac{IB}{qdV}$$

$$n \equiv n(\varepsilon_d, T)$$

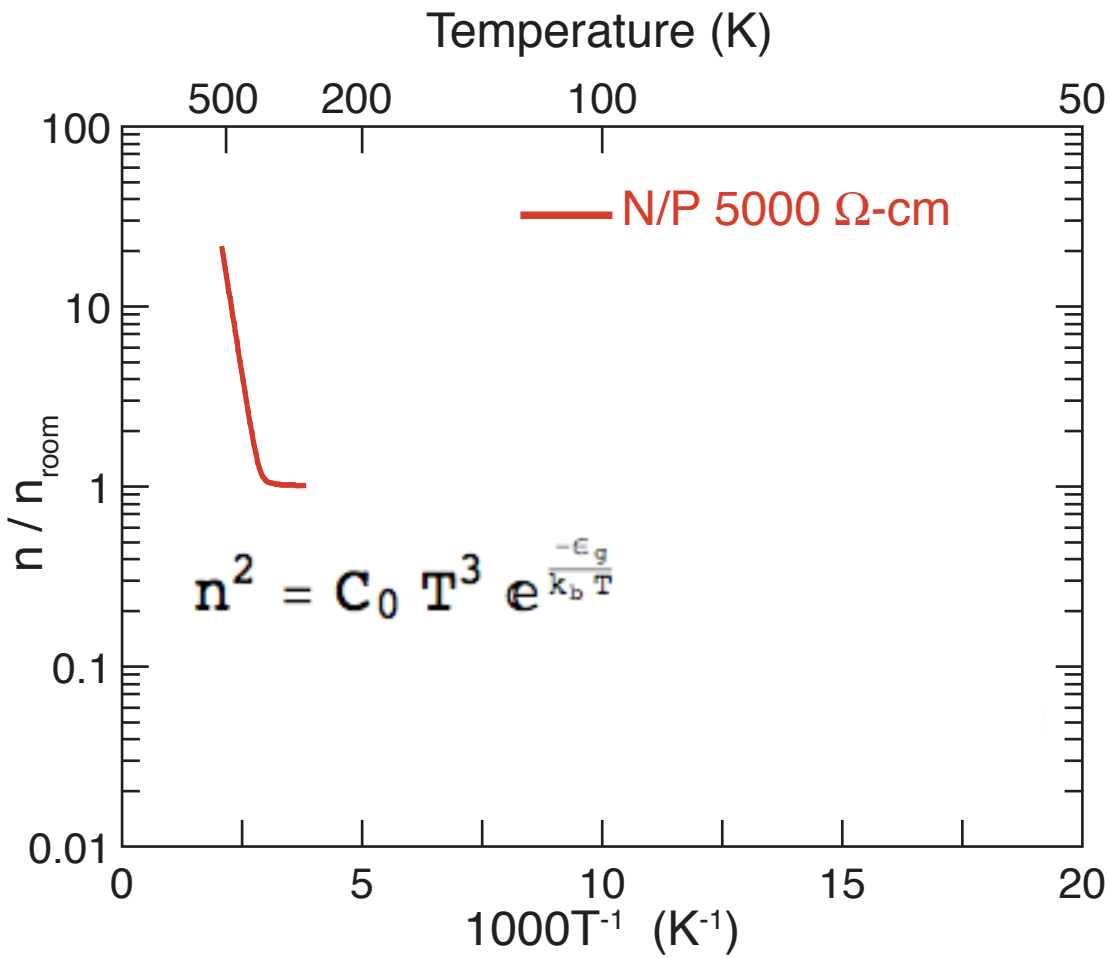


Dopant levels from Hall measurements



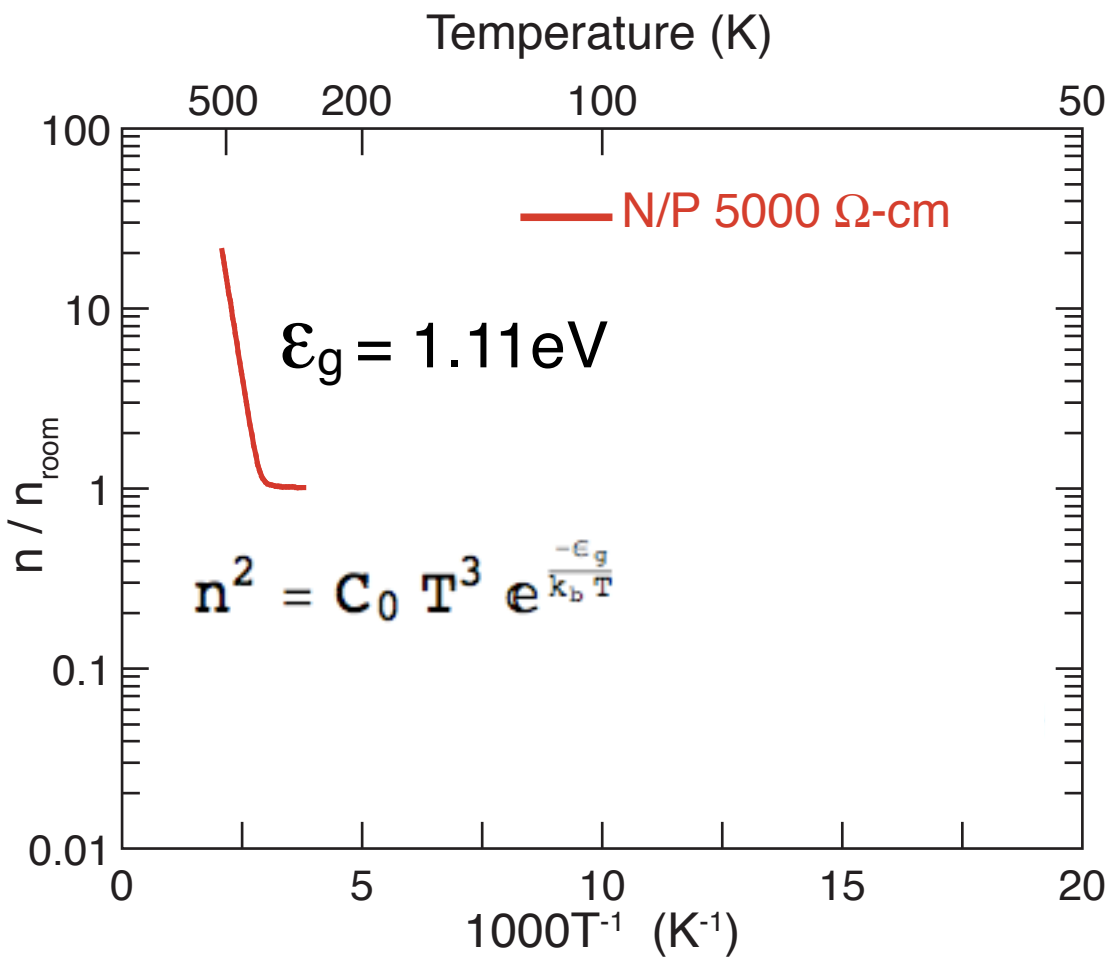
PRELIMINARY RESULTS

Dopant levels from Hall measurements



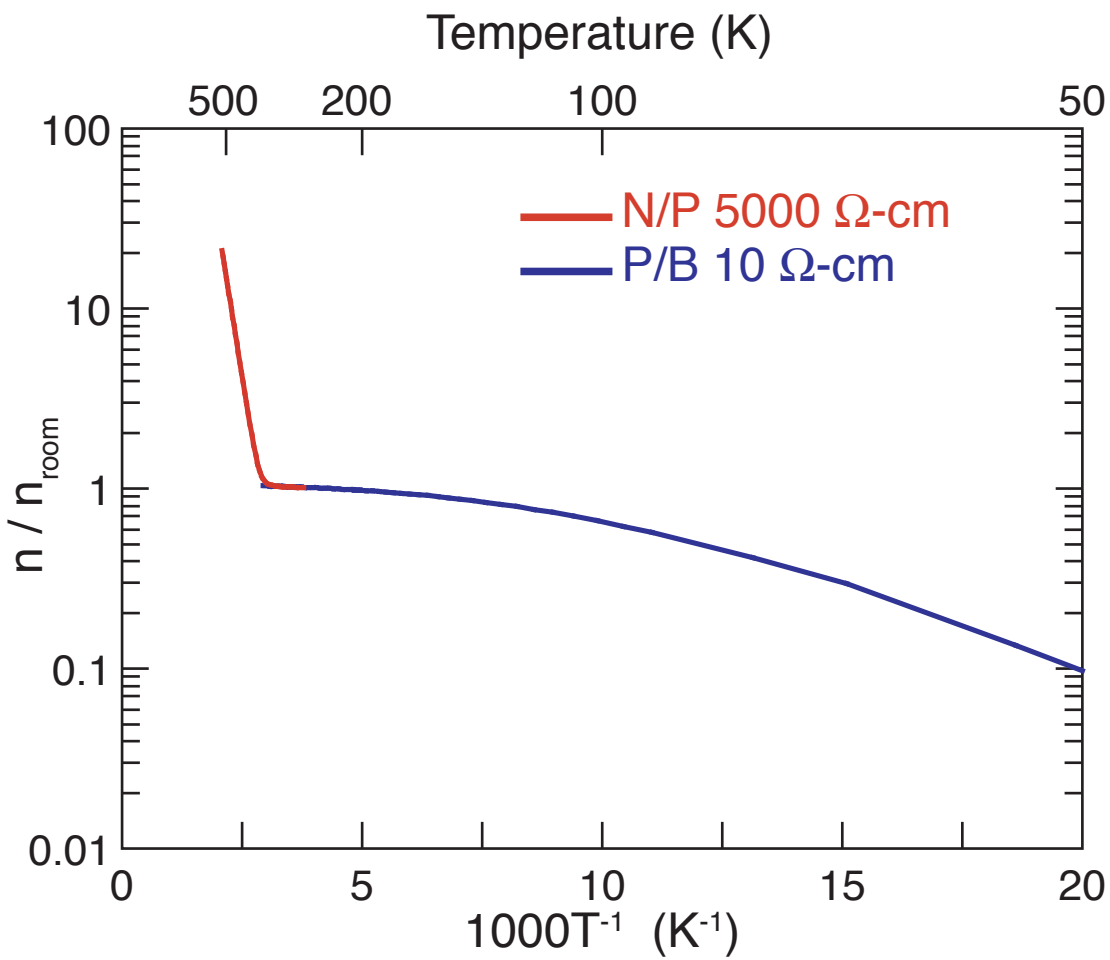
PRELIMINARY RESULTS

Dopant levels from Hall measurements



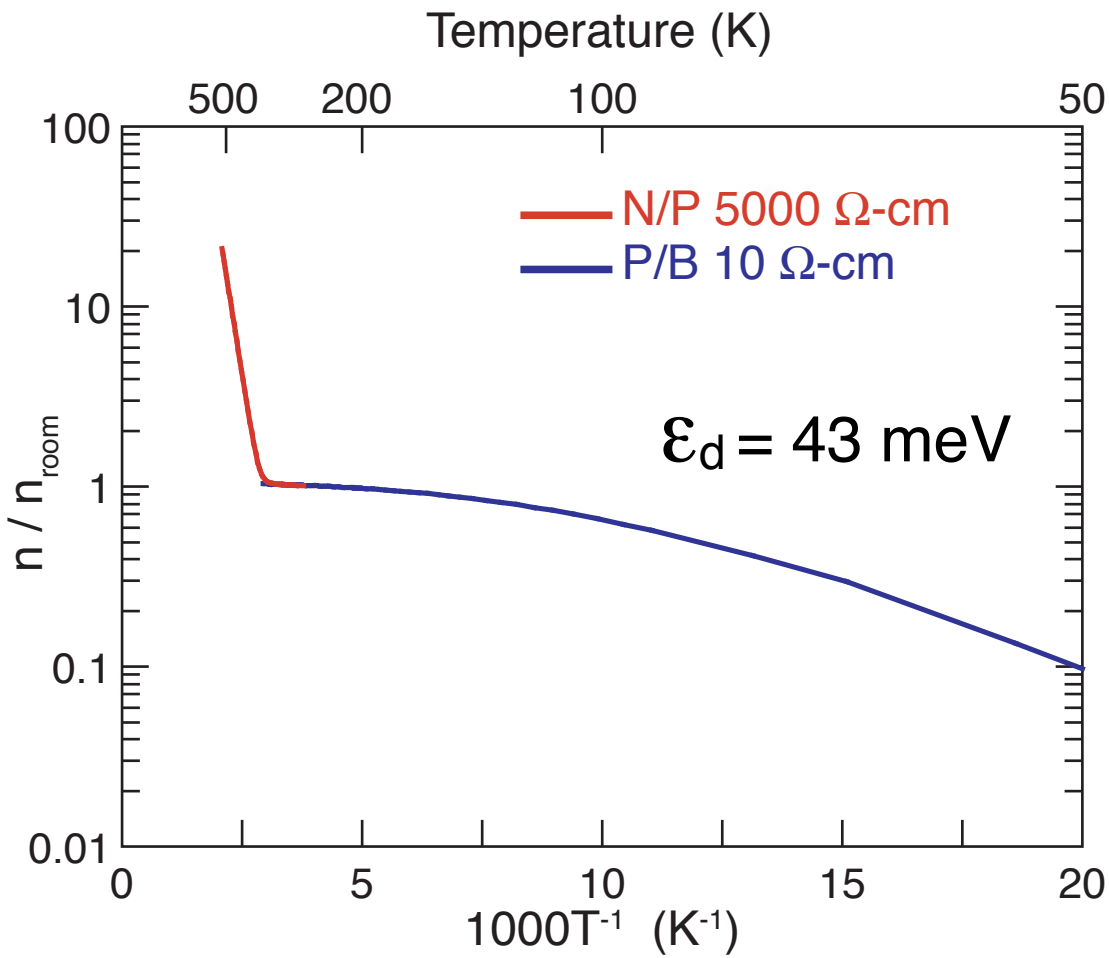
PRELIMINARY RESULTS

Dopant levels from Hall measurements



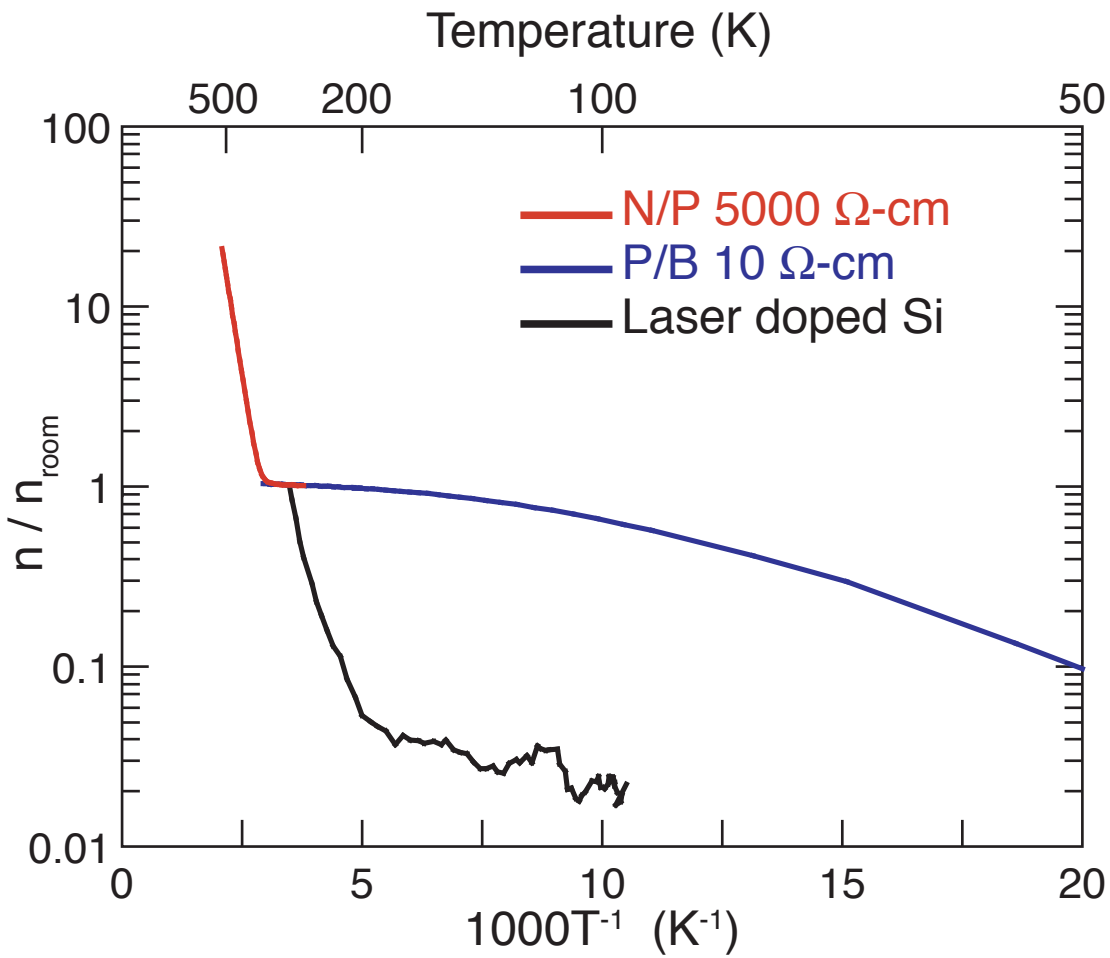
PRELIMINARY RESULTS

Dopant levels from Hall measurements



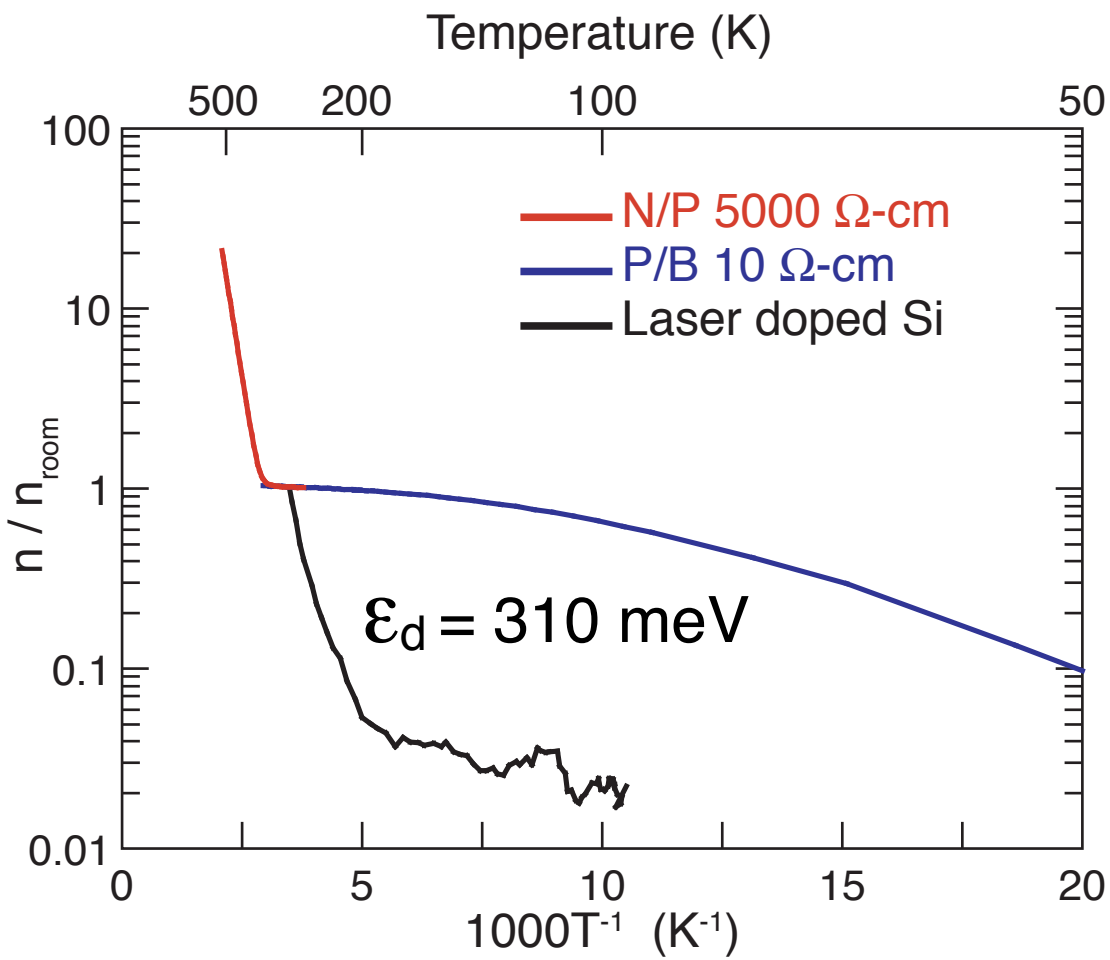
PRELIMINARY RESULTS

Dopant levels from Hall measurements



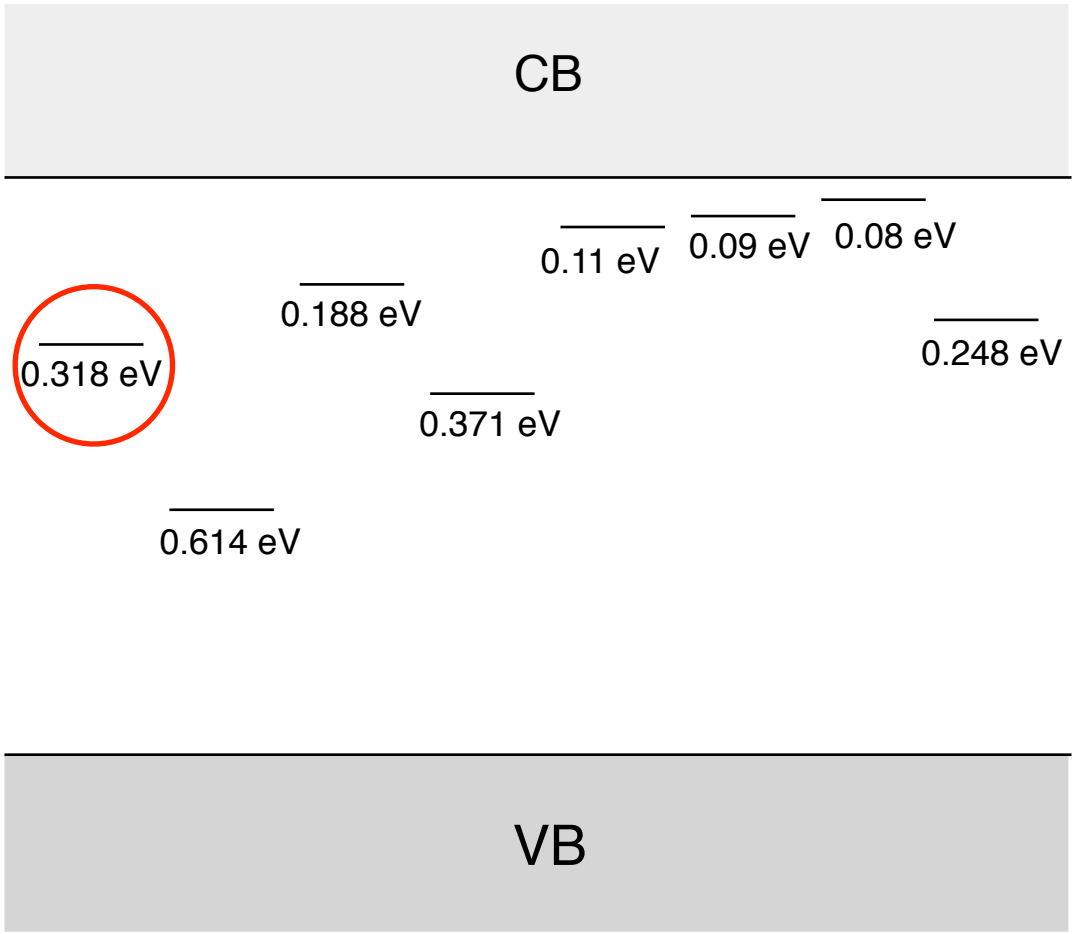
PRELIMINARY RESULTS

Dopant levels from Hall measurements



PRELIMINARY RESULTS

substitutional



Janzén et al. , Phys. Rev. B 29, 1907 (1984)

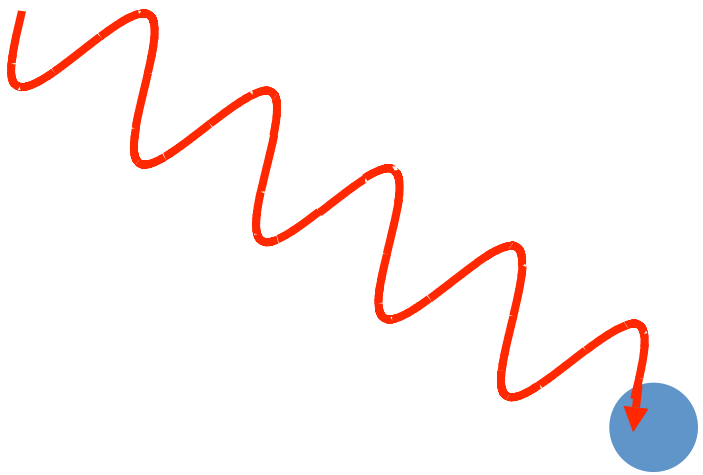
Preliminary data suggests: S takes **substitutional** site

Synchrotron Facilities

National Synchrotron Light Source, Brookhaven, NY

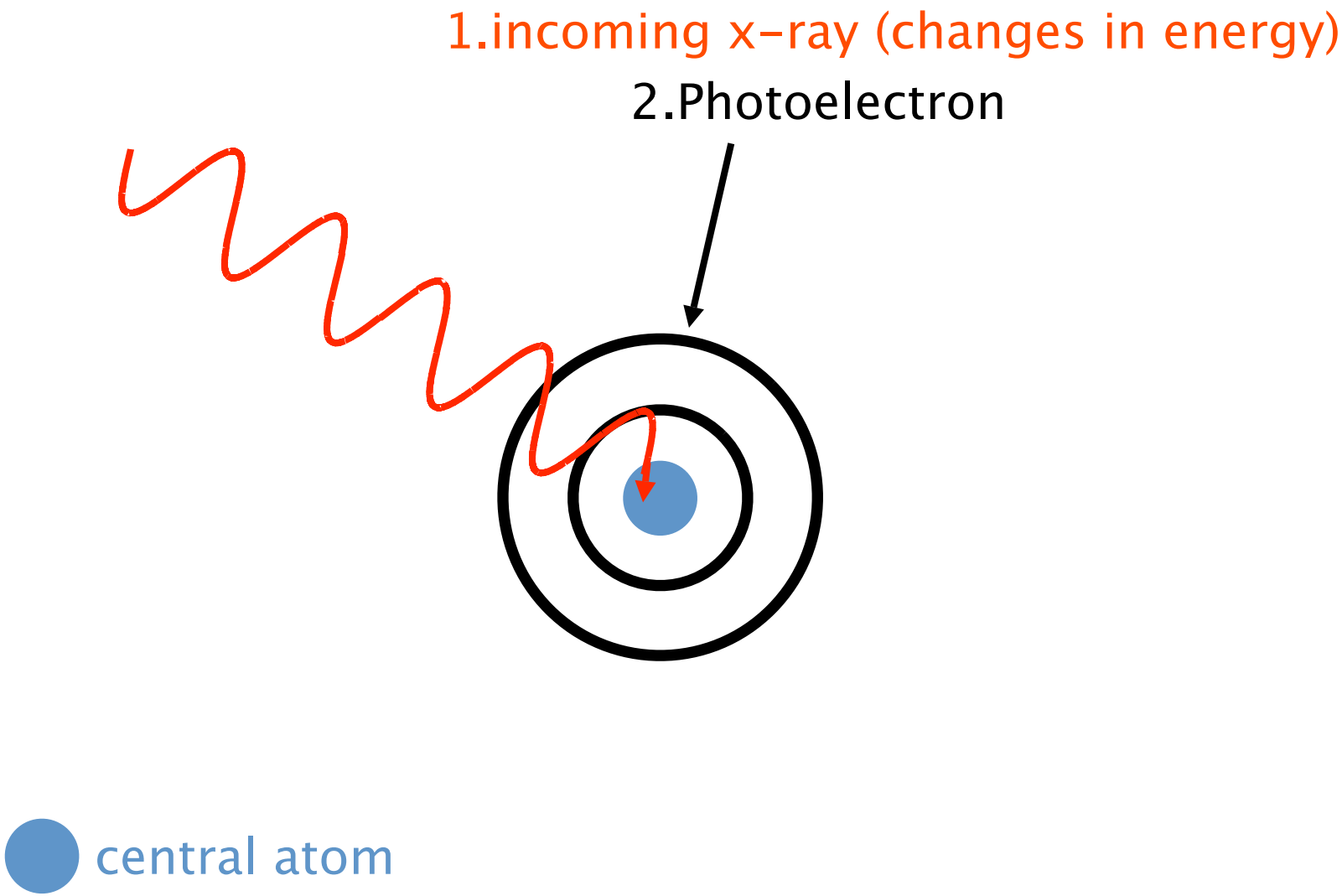
X-ray absorption Spectroscopy: XAS

1.incoming x-ray (changes in energy)

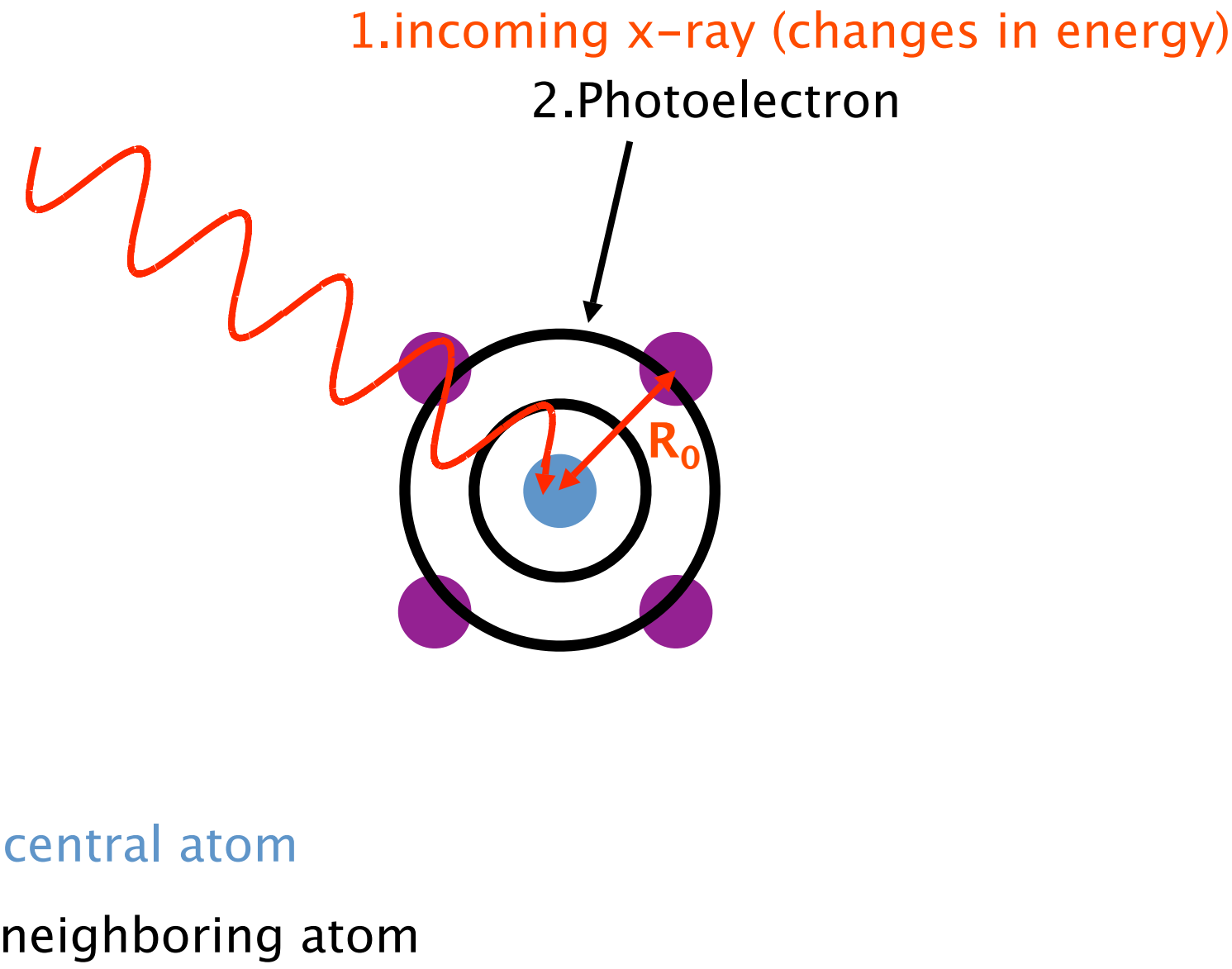


central atom

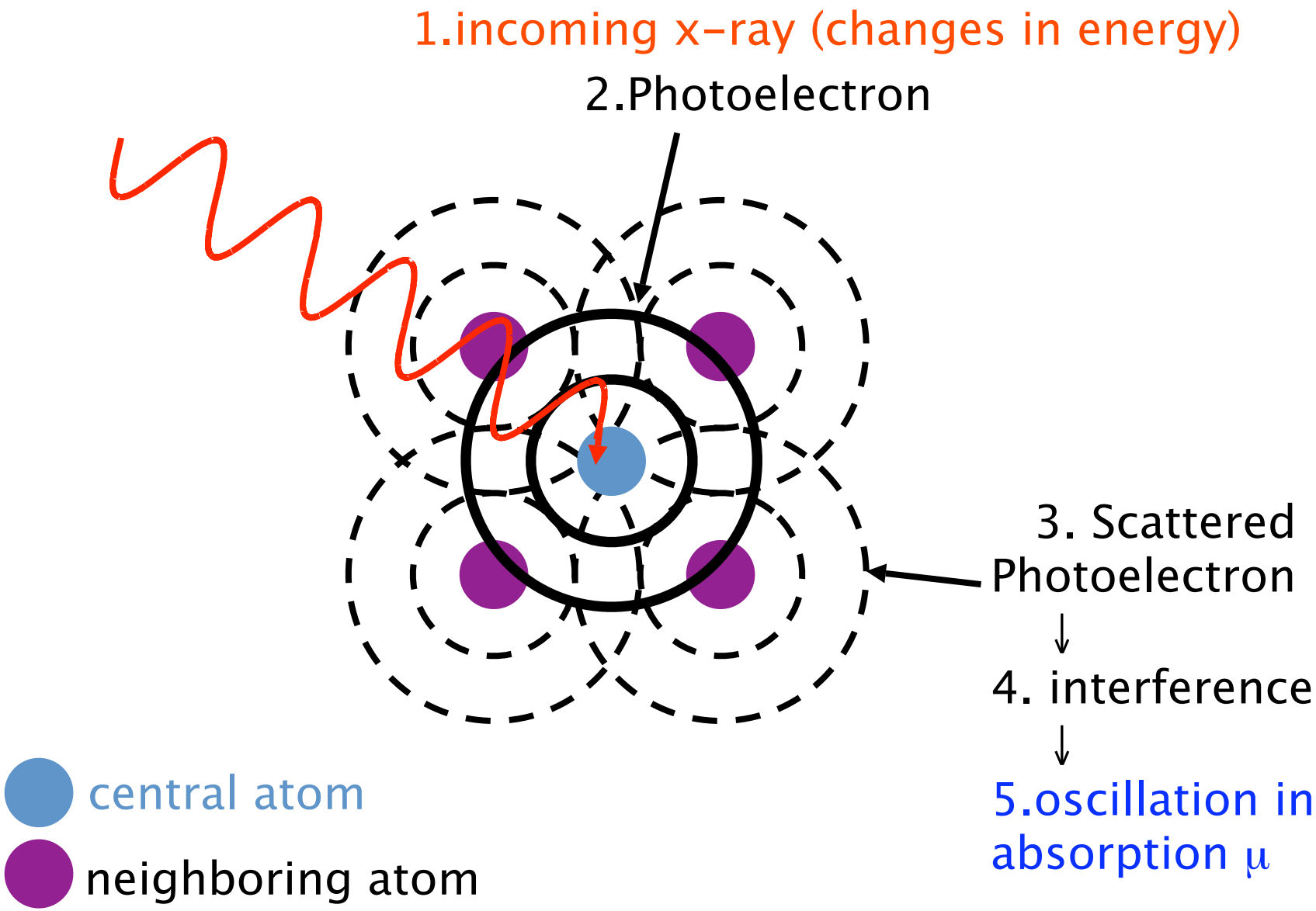
X-ray absorption Spectroscopy: XAS



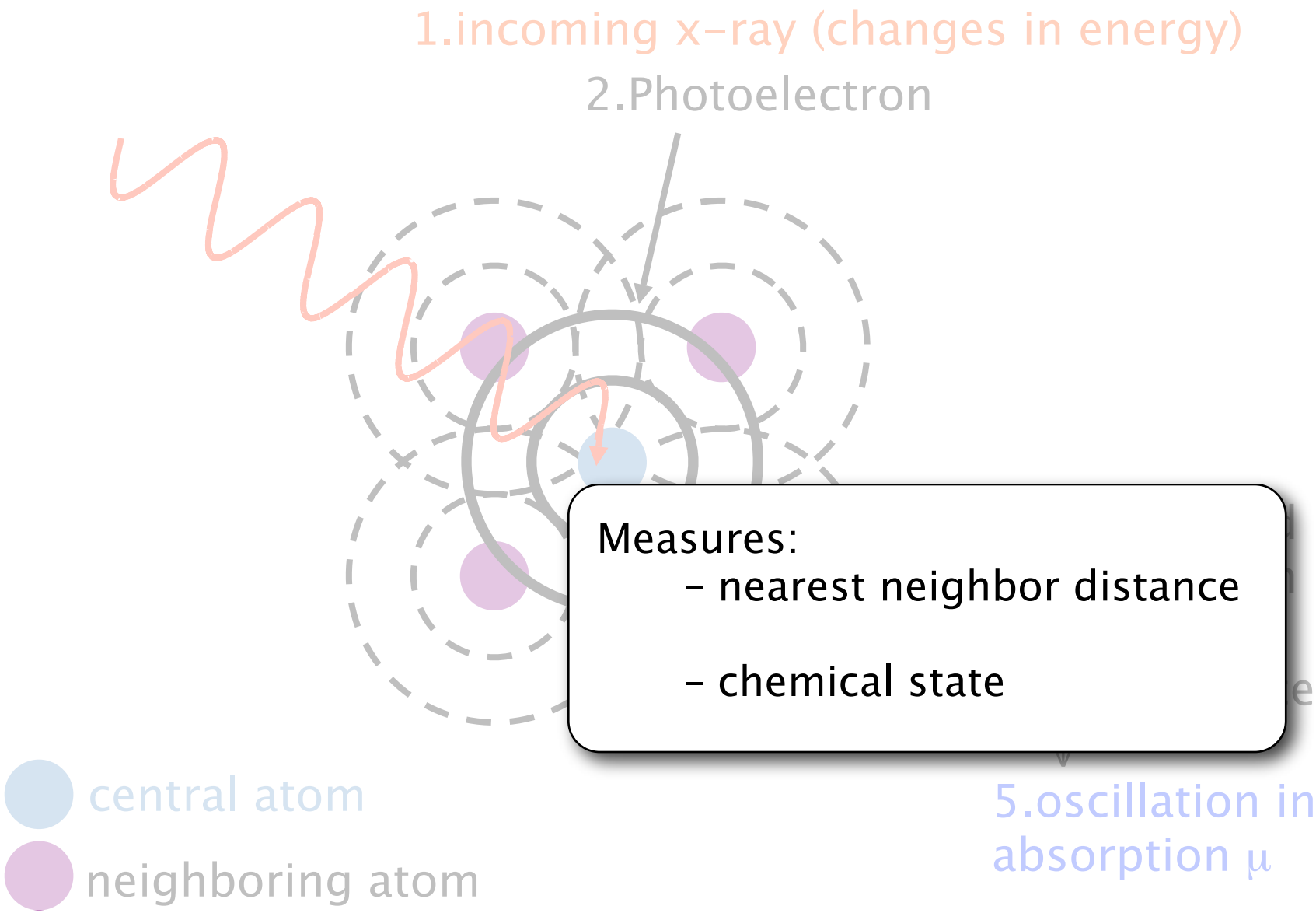
X-ray absorption Spectroscopy: XAS



X-ray absorption Spectroscopy: XAS

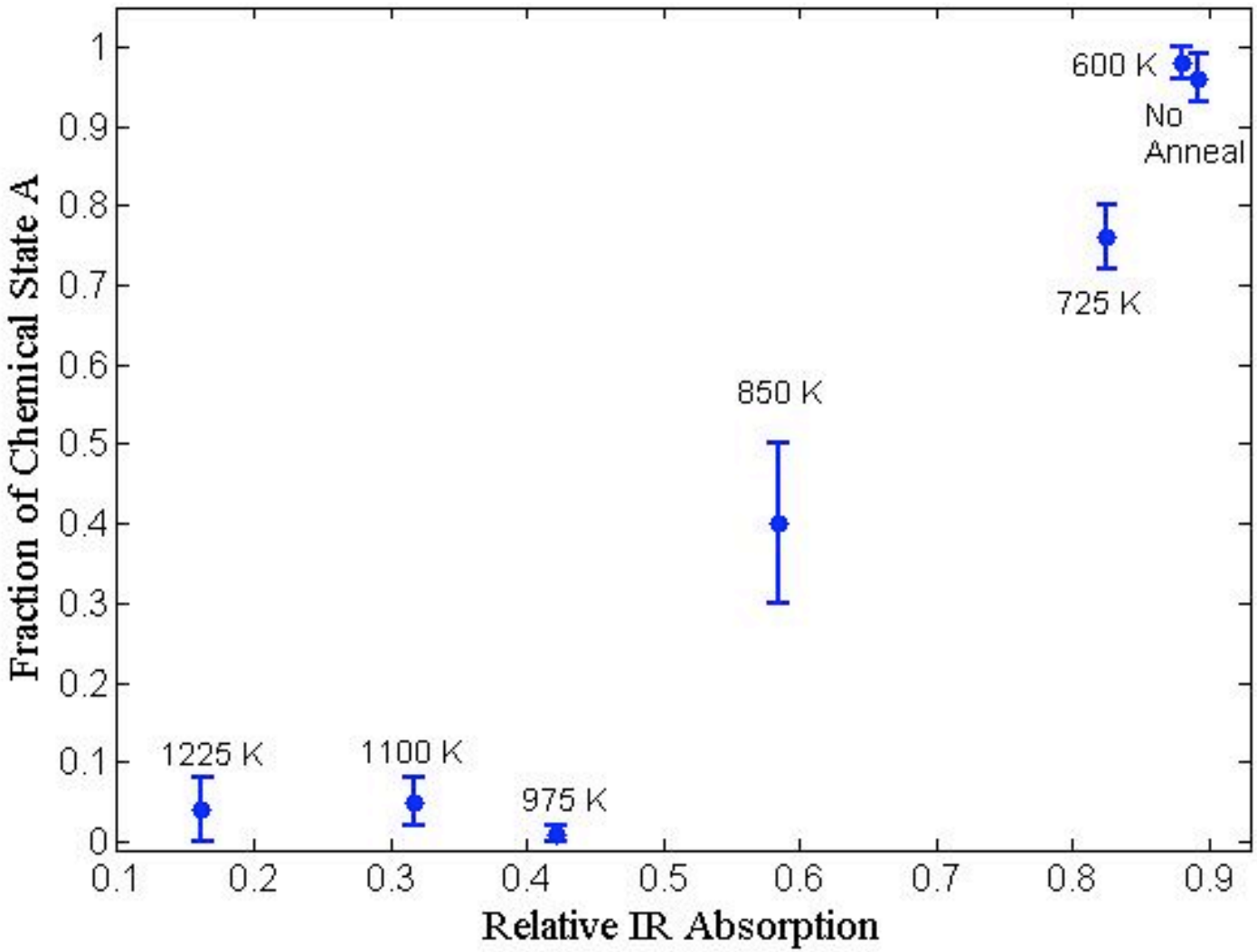


X-ray absorption Spectroscopy: XAS



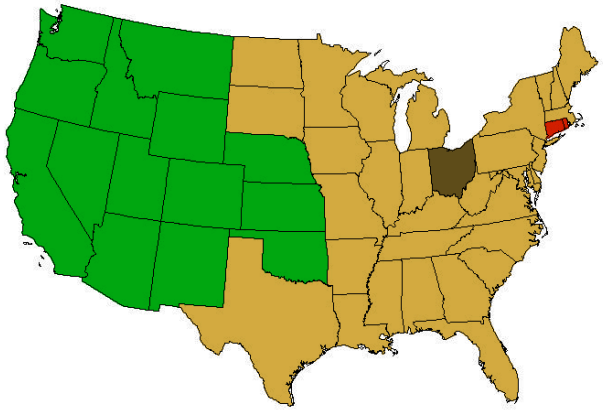
Measures:
- nearest neighbor distance
- chemical state

Tracking Se Impurity Chemical State



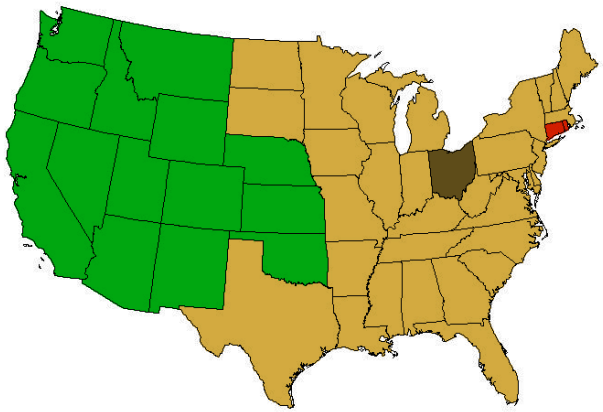
Conclusions

Conclusions

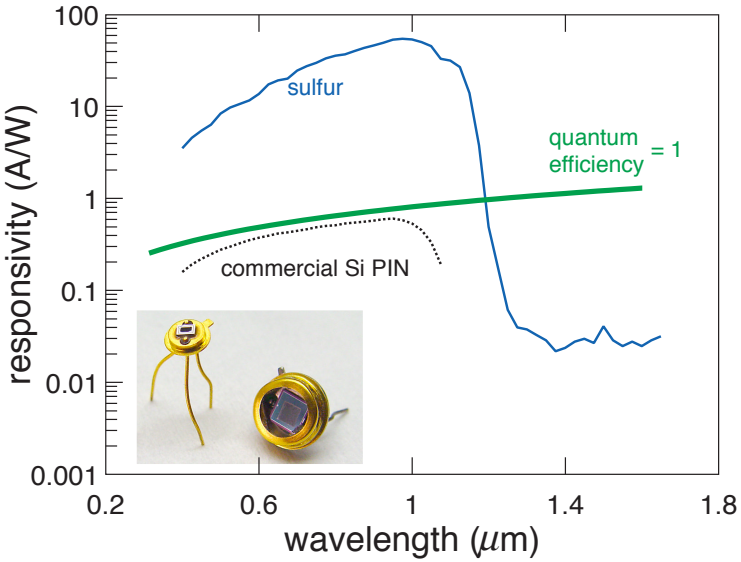


We need to extend silicon's reach

Conclusions

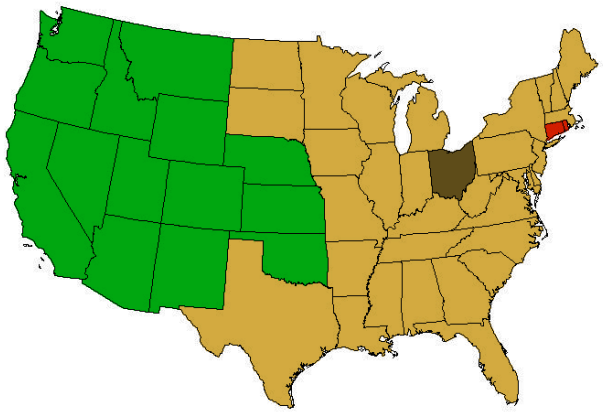


We need to extend silicon's reach



Non-equilibrium doping extends silicon's reach!

Conclusions



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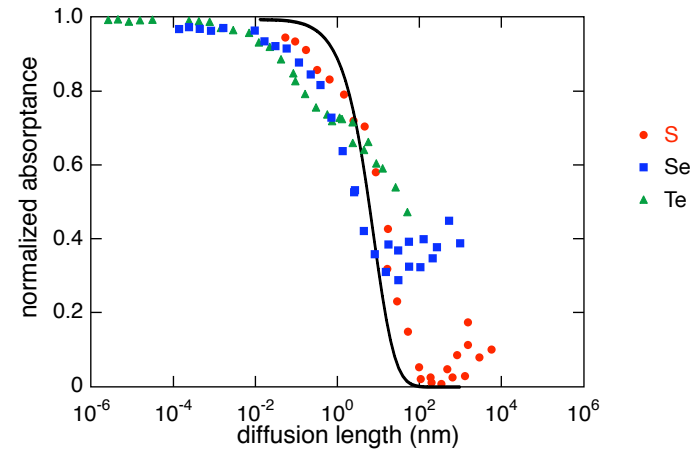
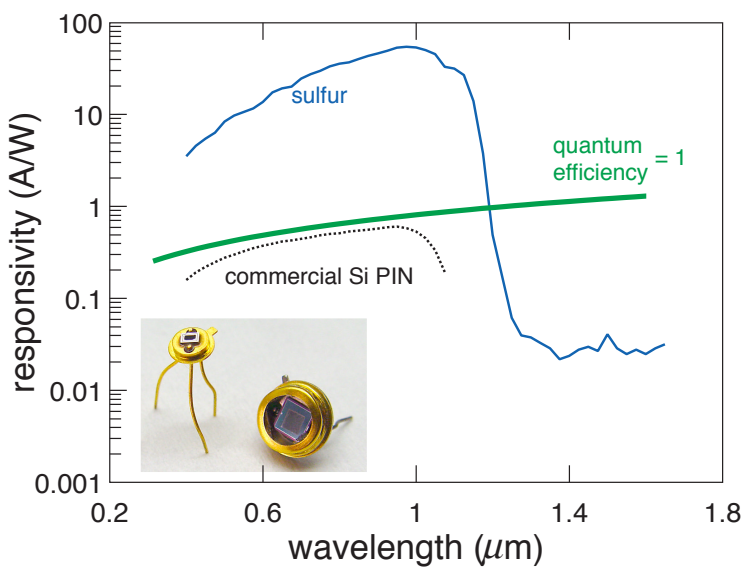
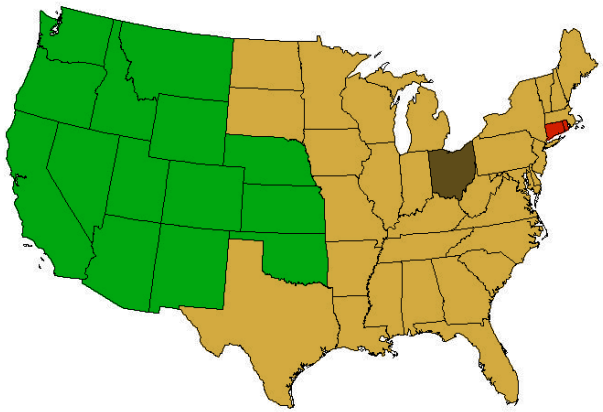


Dopants diffusion governs IR response

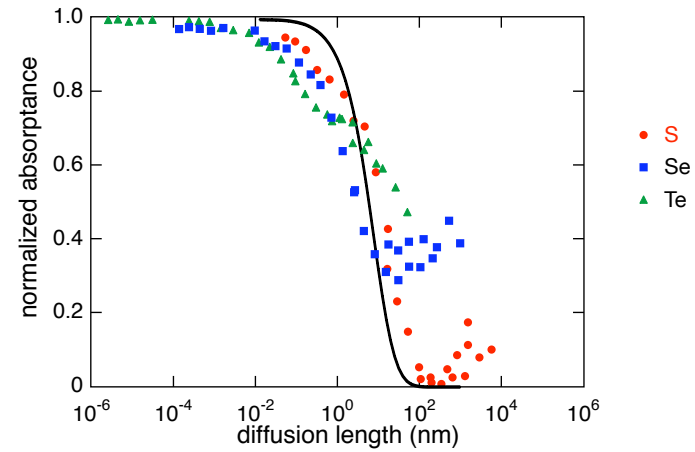


Non-equilibrium doping extends silicon's reach!

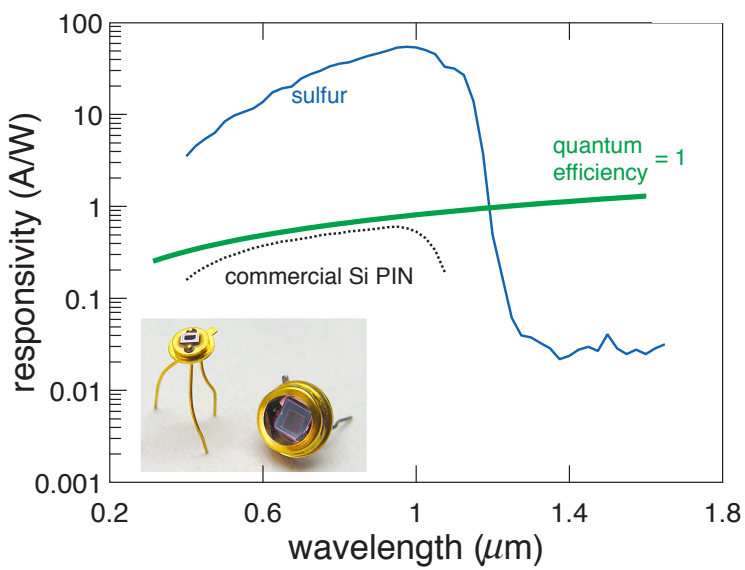
Conclusions



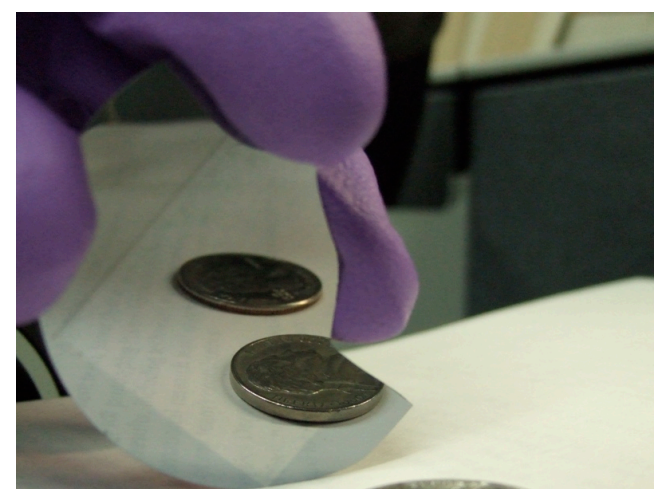
We need to extend silicon's reach



Dopants diffusion governs IR response



Non-equilibrium doping extends silicon's reach!



On our way to solving the puzzle!

Acknowledgements

Meng-ju Sher, Eric Diebold, Albert Zhang,
Jim Carey, Brian Tull, Mike Aziz, Brion Bob

the Mazur Group

Funding: NSF GFRP, ARO

Thanks! Questions?

winkler@physics.harvard.edu

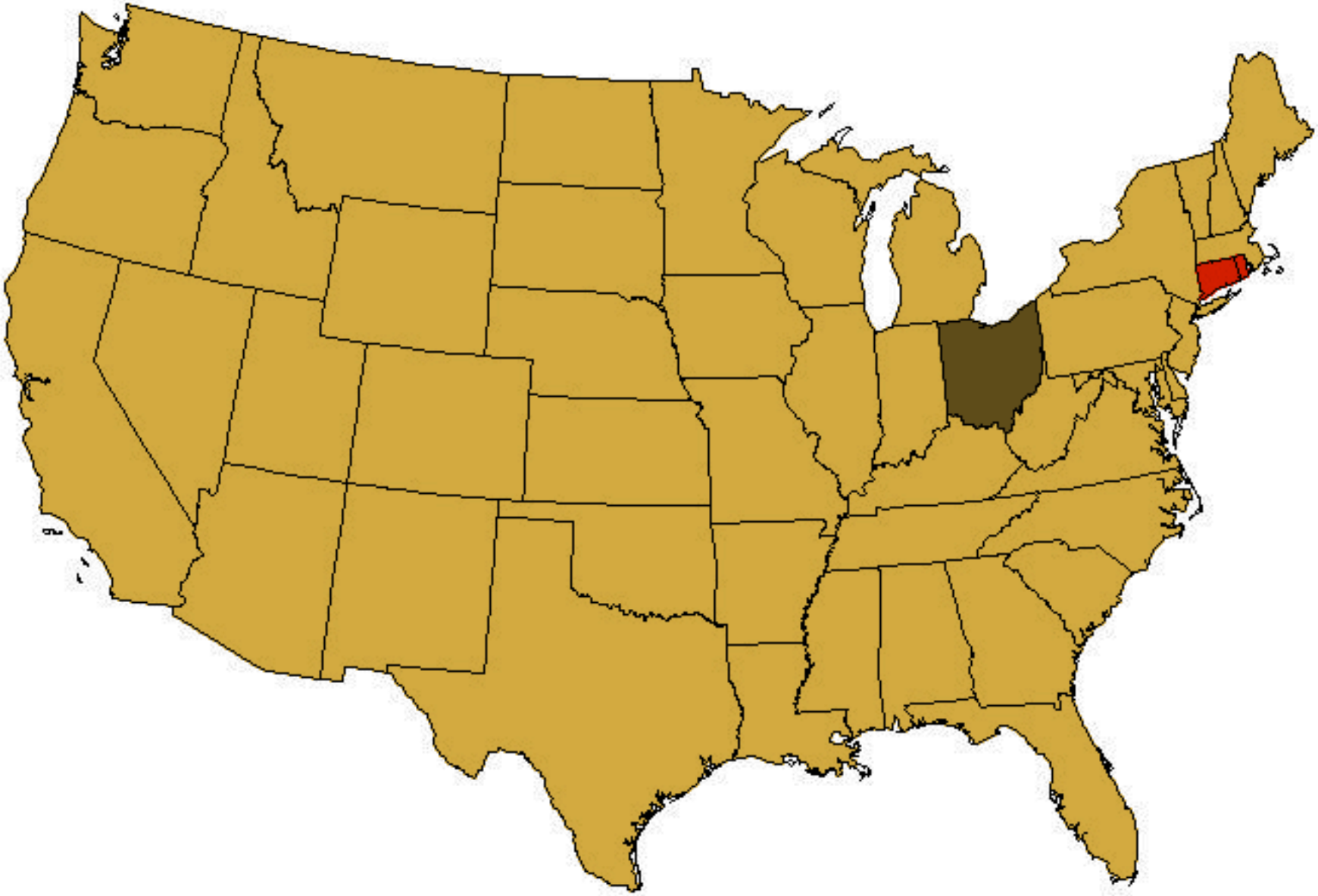
http://mazur-www.harvard.edu

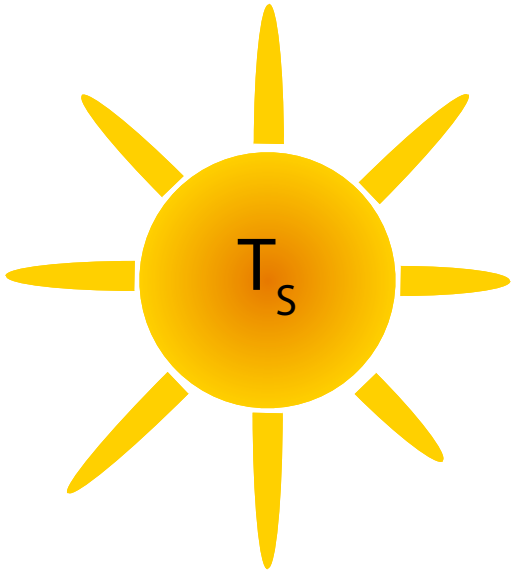
END OF TALK

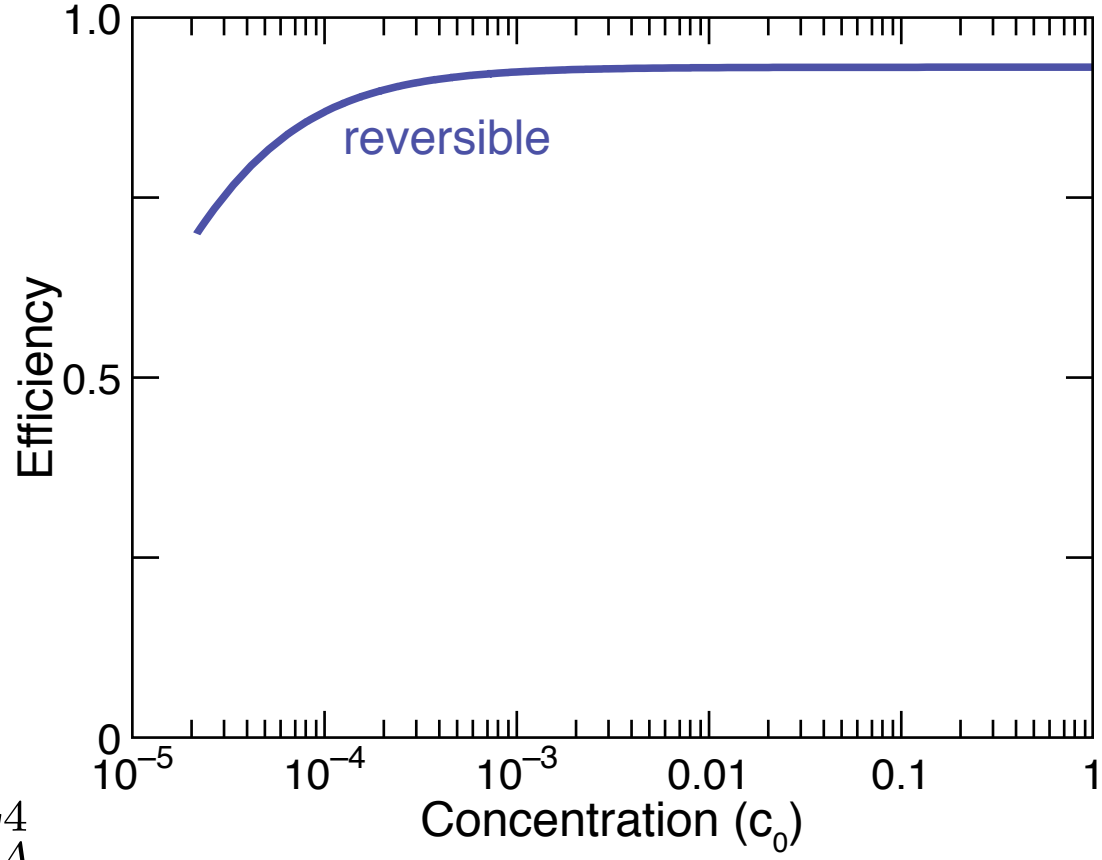
Why extend silicon's reach?

Why extend silicon's reach?

Why extend silicon's reach?





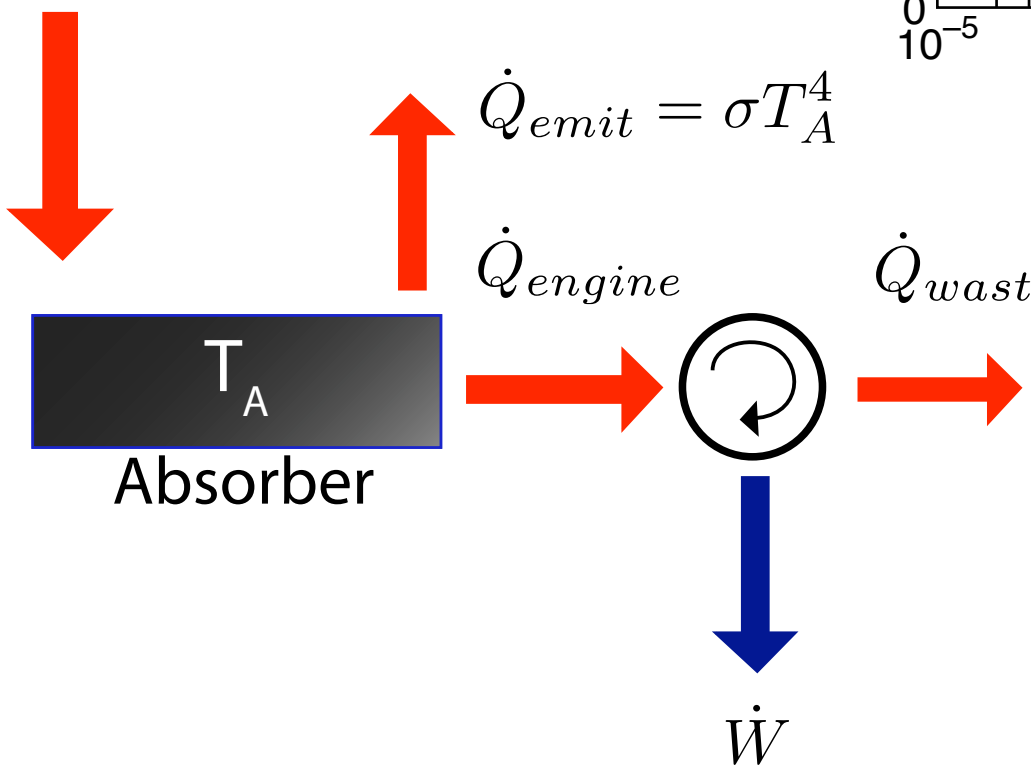


$$\dot{Q}_{sun} = \sigma c_0 T_S^4$$

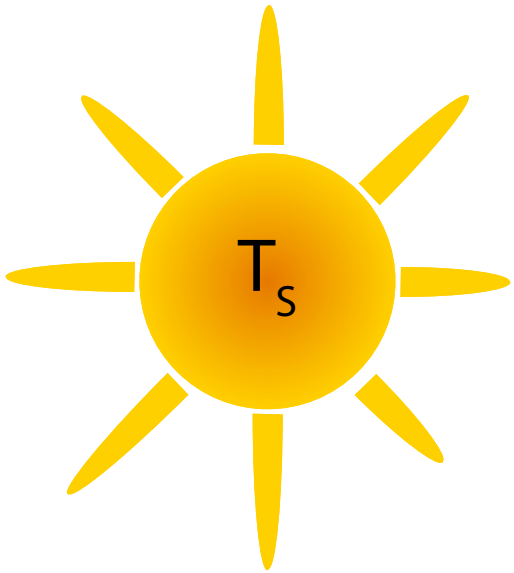
$$\dot{Q}_{emit} = \sigma T_A^4$$

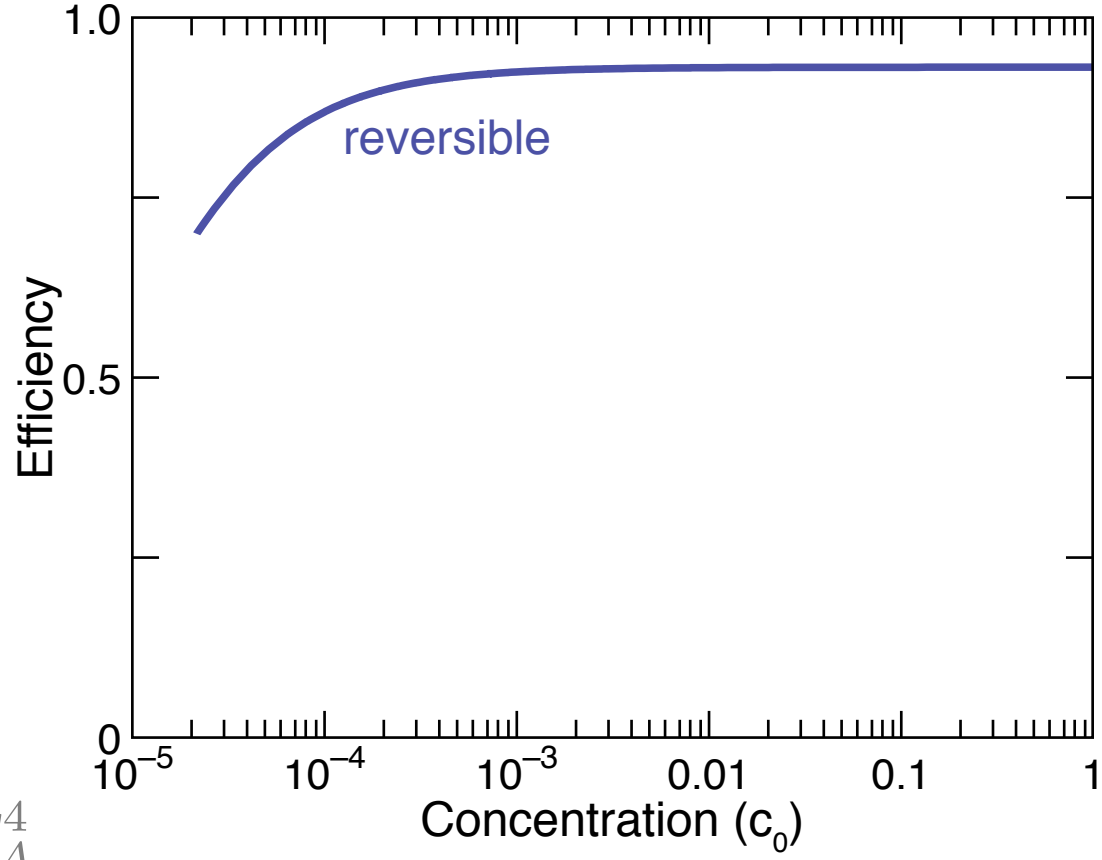
$$\dot{Q}_{engine}$$

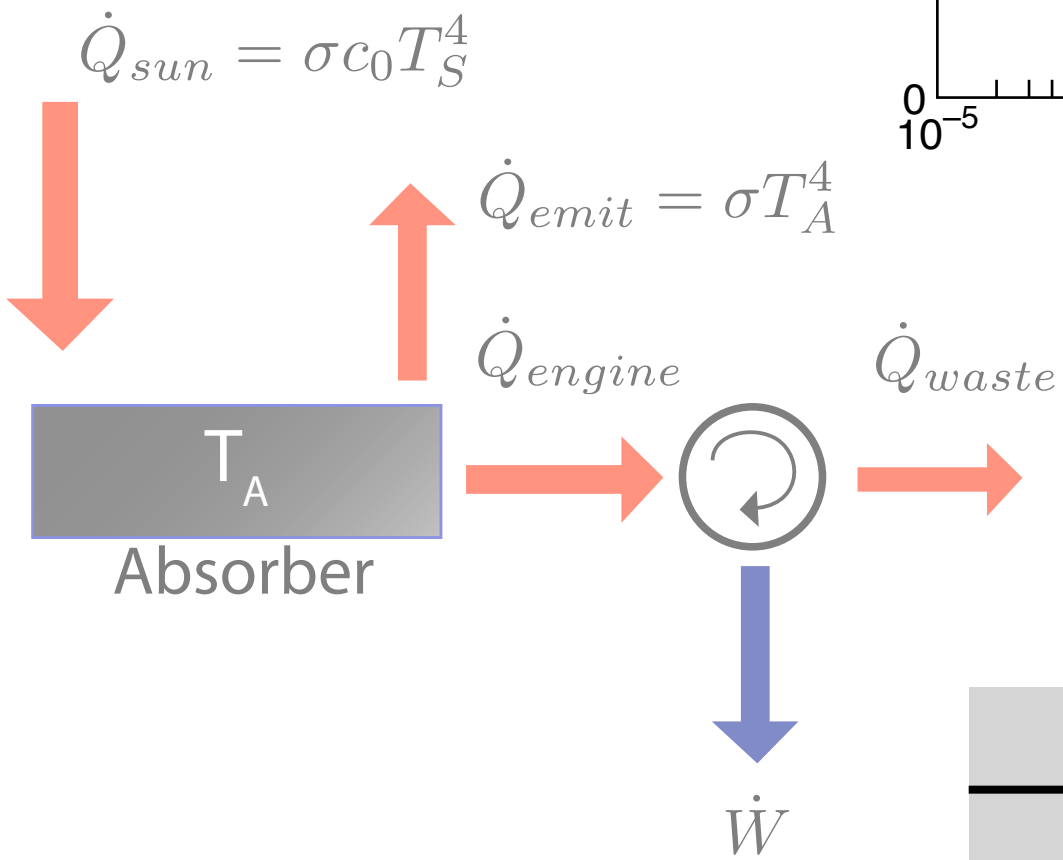
$$\dot{Q}_{waste}$$



$$\eta = 1 - \left(\frac{T_A}{c_0 T_S}\right)^4 - \frac{\dot{Q}_{waste}}{c_0 \sigma T_S^4}$$



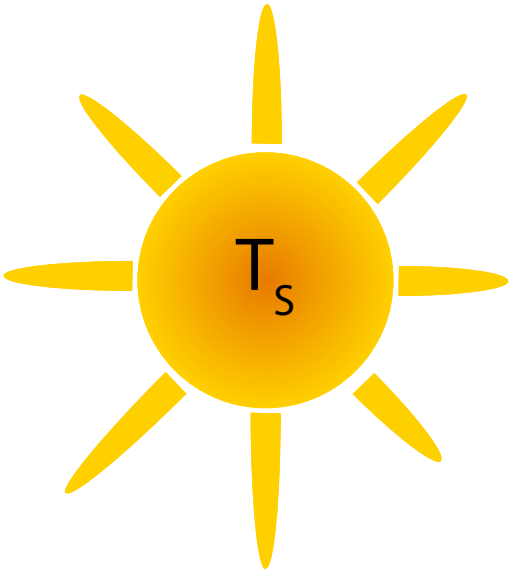


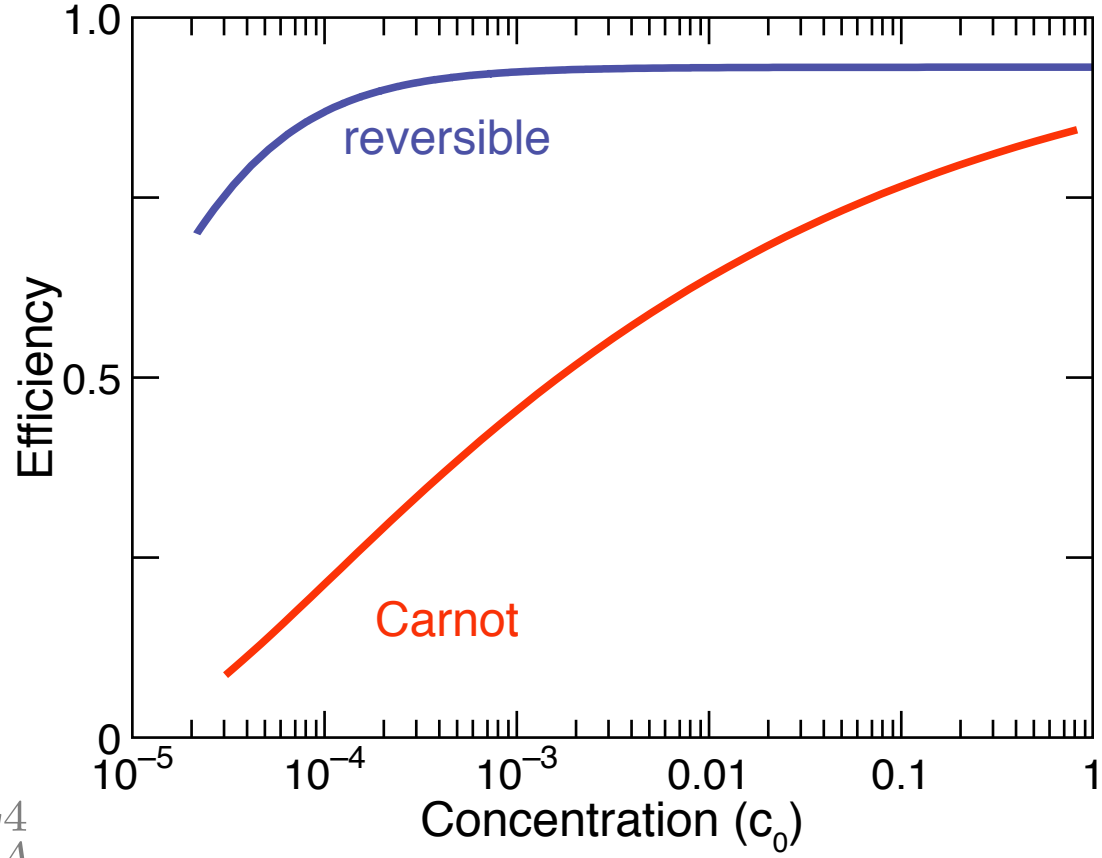


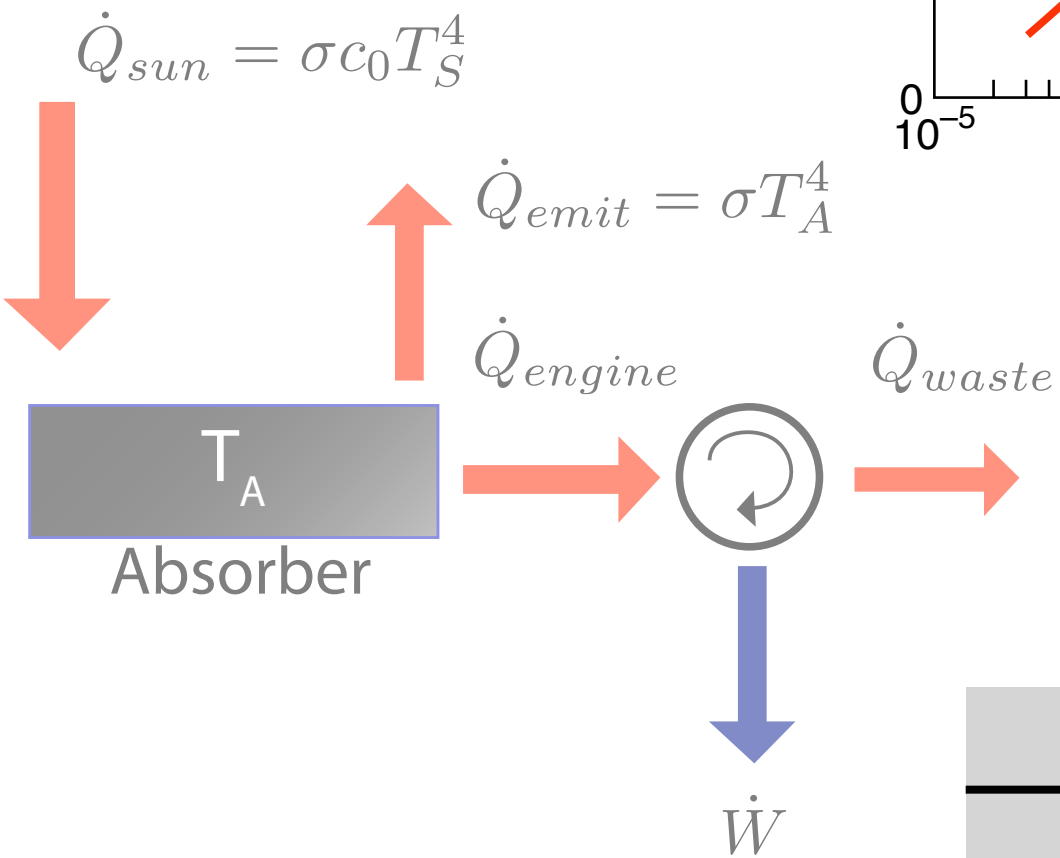
$$\eta = 1 - \left(\frac{T_A}{c_0 T_S}\right)^4 - \frac{\dot{Q}_{waste}}{c_0 \sigma T_S^4}$$

carnot

$$\dot{S}_{engine} = \dot{S}_{waste}$$







$$\eta = 1 - \left(\frac{T_A}{c_0 T_S}\right)^4 - \frac{\dot{Q}_{waste}}{c_0 \sigma T_S^4}$$

carnot
$\dot{S}_{engine} = \dot{S}_{waste}$